THE ANALYST

EDITORIAL

14 Belgrave Square

FROM August 7th, 1874, until June 24th, 1945, the Society and *The Analyst* had no home of their own: the Society's Registered Office was the office or laboratory of the Honorary Secretary of the period, and the journal was edited from beside the Editor's own work-bench. In 1945 the Society took its first premises—one room; but adjacent offices were not available, and as the Society grew it had to rent additional accommodation on another floor, and later in another building. The inconvenience of being so scattered needs no description.

Now, through the kindness of the Society of Chemical Industry, we have moved to a proper home in a suite of offices on one floor of their new premises, 14 Belgrave Square, London, S.W.1. Here at last we have adequate accommodation for all the offices, and a Council or Committee Room of our own. The space is not sufficient to allow us to hold the Ordinary Meetings of the Society at this address, and they will continue to be held in the Chemical Society's Meeting Room at Burlington House.

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ORDINARY MEETING

An Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, December 5th, 1956, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. K. A. Williams, A.Inst.P., M.Inst.Pet., F.R.I.C.

The subject of the meeting was "Trade Effluents," and, after an Introduction by H. N. Wilson, F.R.I.C., the following papers were presented and discussed: "The Determination of Metallic Contaminants," by N. T. Wilkinson, F.R.I.C.; "Analytical Problems Concerned with Oil and Grease in Effluents and River Waters," by J. G. Sherratt, B.Sc., F.R.I.C.; "Trade Effluents Analysis: the Oxygen Demand," by C. J. Regan, B.Sc., F.R.I.C.

NEW MEMBERS

Ordinary Members

Brian Alldred, B.Sc. (Manc.); Douglas Macdonald Watt Anderson, B.Sc., Ph.D. (Edin.), A.R.I.C.; George John Austin, A.R.I.C.; Robert Luman Barnard, M.S. (New Hampshire), Ph.D. (Cornell); John Frederic Bates; Julian Bernal Nievas, M.Sc. (Zaragoza), Ph.D. (Madrid); Frederick William Bernhardt; Roland Edwin Coulson, A.R.I.C.; Eric Cowley, B.Sc., A.R.I.C.; Arthur Raymond Gordon Emslie, M.S.A. (Toronto), D.Sc. (Aberdeen); Edmund English, B.Pharm., B.Sc. (Lond.), F.R.I.C., P.A.I.W.E.; James Horace William Forsythe, B.Sc. (Q.U.B.); Edward Derek France, A.R.T.C.S.; Edmund Frankel, Ph.D. (Vienna); David Austin Giles, B.Sc. (Lond.); Robert Emrys Jones, A.M.C.T., F.R.I.C.; Bernard Elgey Leake, B.Sc., Ph.D. (Liv.); Peter Lindley, B.Sc. (Lond.); Keith Charles Overton; Glenmore Freeman Price, M.Sc. (Wales), Dip.Ed.; John Gerard Reynolds, F.R.I.C.; William McLeod Ross; Luis Serrano-Berges, M.Sc. (Zaragoza), D.Ph. (Madrid); Trevor Gabriel Shute, M.Inst.Gas E; Leslie Singleton, Ph.D. (Leeds), A.R.I.C.; John George Slack, A.R.I.C.; Lloyd Earle Smythe, M.Sc. (Syd.), Ph.D. (Tas.), F.R.A.C.I., A.R.I.C.; Takeo Takahashi, Dr.Eng. (Tokyo); Jacobus Johannes van Zyl; James Andrew Jamieson Walker, B.Sc.; Erwin Gunther Walliczek.

Junior Members

Jeffrey James Cox; John Muir; Alan Charles Wright.

NORTH OF ENGLAND SECTION and PHYSICAL METHODS GROUP

A Joint Meeting of the North of England Section and the Physical Methods Group was held at 6.30 p.m. on Friday, October 19th, 1956, in the Robinson Laboratory, Manchester University. The Chair was taken by the Chairman of the Physical Methods Group, Dr. J. E. Page, F.R.I.C.

The following papers were presented and discussed: "Ion Exchange in the Study of Complexes," by T. V. Arden, B.Sc., Ph.D., F.R.I.C., M.I.M.M.; "Some Recent Application of Ion Exchange in Biochemistry," by T. S. Work, Ph.D., D.Sc.; "The Selective Elution of Metals Adsorbed on Cation-exchange Resins by Organic Solvents. Part II," by R. A. Wells, B.Sc., A.R.I.C., and Patricia J. Macdonald (this paper was presented by Dr. D. A. Everest).

SCOTTISH SECTION

A Joint Meeting of the Section with the Stirlingshire Sections of the Royal Institute of Chemistry and the Society of Chemical Industry was held at 7.30 p.m. at the Lea Park Restaurant, Falkirk, on Tuesday, October 23rd, 1956. The meeting was held under the Chairmanship of Dr. Magnus A. Pyke, F.R.I.C., F.R.S.E., in the dual capacity of Chairman of the Stirlingshire Section of the Royal Institute of Chemistry and Vice-Chairman of the Scottish Section.

The meeting took the form of an exhibition and demonstration of modern analytical apparatus including: "Statistical" Calculating Machine, demonstrated by Mr. R. D. Sutherland and Mr. Liney; "Electronik" Continuous Balance Potentiometer, demonstrated by

Mr. A. T. Hunter; Interference Microscope, demonstrated by Mr. A. M. Tennant and Mr. J. C. Gentles; Proximity Meter, demonstrated by Mr. J. A. Bolton. There was also available for inspection a Caravan Mobile Demonstration Unit, which included equipment for the measurement, control and recording of temperature level, pressure, flow, pH, capacity, sheet thickness, smoke density, moisture content, voltage and current by electronic means.

MIDLANDS SECTION AND MICROCHEMISTRY GROUP

A JOINT Meeting of the Midlands Section and the Microchemistry Group was held at 6.30 p.m. on Friday, October 5th, 1956, in the lecture room of the University Chemical Laboratory, Pembroke Street, Cambridge. The Chair was taken by the Chairman of the Midlands Section, Mr. J. R. Leech, J.P.

The subject of the meeting was "Sub-micro Methods in Inorganic and Organic Analysis," and the following papers were presented and discussed: Introduction by R. Belcher, Ph.D., D.Sc., F.R.I.C.; "General Review of Sub-micro Methods," by T. S. West, B.Sc., Ph.D., A.R.I.C.; "The Determination of Alkoxyl," by M. K. Bhatty, M.Sc., A.R.I.C.; "The Determination of Nitrogen," by M. Williams, B.Sc., A.R.I.C.; "The Determination of Iodine," by A. R. Shah, M.Sc., A.R.I.C. (see summaries below).

The meeting was preceded at 2 p.m. by a visit, by kind permission of Messrs. Fisons Pest Control Ltd., to their Research Station at Chesterford Park.

INTRODUCTION

DR. R. BELCHER said that when micro methods of organic analysis were first developed by Pregl, micro methods of inorganic analysis, pioneered by Emich, had been available for several years. The problems involved were different, and were usually more difficult in organic microanalysis, but in most cases the end of the organic determination was essentially inorganic and so organic microanalysis owed much to its inorganic counterpart.

In this series of papers the authors were going to describe some of their investigations in the field of what was termed sub-micro (or, if preferred, microgram) organic analysis. The corresponding inorganic technique had also preceded this by several years, when the work done on the transuranic elements was revealed after the War, but the authors felt that in developing their technique they owed much less to inorganic sub-micro analysis than they did to the pioneer researches of Pregl and Emich, who showed how to track down errors arising from reduction of the scale of working.

Dr. Belcher continued that his own part in this series of papers was to show briefly the origins of the work and to point out its possible applications. Dr. West would then survey some general methods, but would make special reference to the balance they had developed. They had ventured to call this series of papers "organic and inorganic sub-microanalysis" because the end-determinations were purely inorganic and could be applied without modification in that field. The other speakers would describe particular determinations.

This work had been planned several years ago, and in the first instance had been projected as a piece of academic work to see how far the sample weight could be reduced whilst the accuracy of micro methods was still maintained. But it was quickly realised that if such a technique could be developed it would have far-reaching practical applications. The investigation had therefore been planned on a long-term basis, and no announcement of the results was to be made until several methods were available and the whole system was on a firm basis. They considered that that position had now been reached.

A sample weighing 50 μg was considered to be a suitable amount on which to base the methods; this amount was just visible to the naked eye and would therefore be the lowest practical amount that could be taken without resort to magnification methods.

In planning this work it had been decided to keep the apparatus simple and to avoid "gadgetry" as far as possible. The first problem had been to devise a simple robust balance that would not only weigh accurately in the region required, but also could be produced commercially at a reasonable price. This balance, in conjunction with the syringe burette, were the two main arms of this system of analysis; both were

or would be available commercially. Any other apparatus that was required, as it was in certain determinations, could be constructed readily by a competent glass-blower. Hence he thought the claim to have kept the technique simple was justified. He stressed that this work was far from complete; many methods still remained to be perfected, and those that were to be described later represented some that were considered to be reasonably satisfactory.

In conclusion Dr. Belcher added that in no circumstances were they suggesting that this new technique should replace the conventional micro methods. Its application was to cases in which the available sample was limited in amount or in which the material was very precious. Probably its main application would be in physiological chemistry and biochemistry.

General Review of Sub-micro Methods

Dr. T. S. West said that the region of ultra-micro analysis was regarded as that in which the sample weight was less than 100 μg. Titres could usually be kept in the region of 50 to 200 μl, and the volumes of titration media less than 2 ml. It was usually possible to weigh in the true ultra-micro region (50-μg samples) and to finish the determination gasometrically or titrimetrically in a manner that did not require special manipulative abilities.

A quartz-fibre torsion balance that could be used for the accurate routine weighing of 50-μg samples had been developed at Birmingham University; it was robust and was in most respects simpler to use than a microbalance.

Early titrimetric methods on the sub-micro scale had been devised by Benedetti-Pichler, Wigglesworth and others. Those early methods had required a high degree of manipulative control. The isothermal-distillation technique of Conway, Kirk and co-workers had found some applications. Other methods that had been described by Kirk, Kuck, Kirsten and Unterzaucher were not generally applicable to the ultra-micro scale of working. The application of physical methods of end-point detection to ultra-micro titrations might be of considerable value. The use of complexometric titration, ion-exchange resins and non-aqueous titrimetry had been exploited with some success on this scale of working.

The Determination of Alkoxyl

Mr. M. K. Bhatty described the development of a sub-micro method for the determination of alkoxyl. A sample weighing approximately 50 μg was used, and the accuracy attained was the same as that of the micro or semi-micro method. The decomposition followed the classical Zeisel method, but the Vieböch - Brecher amplification titration was applied.

The main problem in the development of the method was the elimination of sources of error insignificant at higher scales of working. Among these were the efficiency of absorption of the alkyl halides, the efficiency of the scrubbing of the gas stream, the age of the scrubbing solution and the rate of distillation. The main source of error was the diffusion through the rubber connections of organic vapours normally present in the laboratory atmosphere in minute amounts. All these sources of error had been eliminated, and the method had given excellent results for a wide range of alkoxyl contents.

The Determination of Nitrogen

Mr. M. Williams said that nitrogen could be determined satisfactorily on samples weighing about 50 μg by decomposition in a sealed tube at 420° C. The ammonia formed was titrated in the digest with sodium hypochlorite; transference was avoided by using the digestion tube as the titration vessel. The technique had also been applied to compounds that required pre-reduction in the conventional procedure. Some compounds did not give a complete recovery of nitrogen, and the reducing agents so far tried did not make any significant improvement; work on this aspect was in progress.

The Determination of Iodine

Mr. A. R. Shah said that iodine could be determined on 50-μg samples by fusion with metallic sodium in a sealed tube and then applying the Leipert amplification titration. This general decomposition procedure was being applied to other elements, so that alternative methods would be available to suit a particular set of circumstances. There was little trouble with the method when nitrogen was absent; in its presence cyanide was formed and a number of side-reactions occurred during the oxidation of iodide with bromine water. Several methods of overcoming this interference had been tried, and the most successful appeared to be the expulsion of cyanide by boiling in an acetic acid medium.

The Investigation of Various Chemical Systems by Electron-spin Resonance

By D. J. E. Ingram

(*Presented at the meeting of the Physical Methods Group on Friday, May 25th*, 1956)

In this paper the application of electron-resonance techniques to the study of different chemical problems is briefly outlined. Although the most direct use of this technique in chemical analysis is for the determination of very small concentrations of paramagnetic atoms, it can also be applied to a large number of other systems that normally contain unpaired electrons or can be easily made to do so. The general conditions governing its applicability are first outlined and then some of the more important cases, such as photochemical reactions, irradiation chemistry and the like, are treated in some detail. The type of chemical information that can be obtained in each case is also summarised and particular importance is attached to the hyperfine-structure analysis, which can often give a wealth of chemical data.

In principle the method of electron resonance[1,2,3] can be applied to any system containing unpaired electron spins, although the width of the resulting line must also be considered to ensure that the absorption can in fact be detected. The lines can usually be made sufficiently narrow either by diamagnetic dilution to reduce the spin - spin interaction or by working at low temperatures to reduce the spin - lattice interaction. The technique can then be used to detect the presence of unpaired electrons at concentrations as low as 10^{12} per g, and also to obtain information about their interaction with the surrounding atoms.

The most direct analytical application of this technique is therefore to transition-group elements and their compounds. The unpaired electrons of the inner unfilled shells give a permanent magnetic moment to these atoms and in most cases they can be directly detected and estimated in quantities down to 10^{-12} g. The different paramagnetic atoms or ions can be readily distinguished from each other by two features of the absorption spectrum. The first is by way of the "g-value," which is effectively the ratio of microwave frequency to magnetic field required for resonance. This will have the free electron-spin value of 2·0023 for an unbound electron, but for electrons associated with the orbitals of any particular atom considerable admixture of the orbital momentum usually occurs so that this "g-value" can take on values ranging from 0·9 to 6·0 or more. The value is usually specific within certain limits to particular atoms and can thus be used as an aid to analysis. The other feature of the spectrum is even more specific and can be of very great analytical importance, *i.e.*, the hyperfine structure that arises from the interaction of the unpaired electron with the magnetic moment of a nucleus around which it is moving. This is considered in more detail under "Hyperfine Structure in Chemical Analysis," on p. 684, but it may be noted that a simple counting of the equally intense hyperfine components will usually identify the particular atoms present immediately. The study of normal paramagnetic atoms has already been dealt with at some length by various authors[1,2,4] and so will not be treated in detail in this paper.

There are, however, other particular applications to which electron resonance can be applied, and those that are of considerable practical importance include the study of irradiation chemistry; of impurity concentrations in semi-conductors; the investigation of electron mobility in organic compounds; the study of transient oxidation products; and also the detailed structural analysis that can often be obtained from the angular variation of the spectra. The investigation of each of these systems will now be considered briefly from the point of view of particular experimental problems and the resulting chemical information. The case of photochemically formed radicals has been chosen first, since this is a widely applicable technique.

The study of photochemically formed radicals

If the bond joining two atoms in a molecule is broken, an unpaired electron will normally be left on each of the two resulting fragments. The lifetime of these radicals is usually extremely short, as they will quickly react to re-form the original molecule. If, however, some means can be devised of holding these radicals apart, once they have been formed, they can be detected by electron-resonance techniques, and will give spectra in the same way as normal stable radicals. One possible method of trapping the radicals is to irradiate a solution that has been frozen to form a glass. If the bond is then broken by absorption of suitable radiation, the two pieces of the molecule will fly apart with any excess of energy left, and in so doing will melt the glass along their path. The glass structure will then re-form behind them so that when the excess of energy from the absorbed quantum has been expended the two molecular fragments are left frozen into the glass structure and are incapable of reacting with each other. There are three necessary conditions for this method to work satisfactorily, *i.e.*—

(*i*) the glass structure should be sufficiently strong to prevent the photochemically formed radicals moving once they have expended their initial excess of energy,

(*ii*) on the other hand the glass structure should not be too rigid or the fragments will never fly apart, and

(*iii*) the energy of the absorbed quantum should be such as to break the bond and give sufficient kinetic energy to the resulting fragments.

It can be seen that a careful compromise must be made to satisfy both conditions (*i*) and (*ii*), and it is for this reason that a glass-like structure is always used instead of a crystalline lattice.

When considering possible glass-type structures in which to dissolve the molecules under investigation, it would appear that the most generally useful are those formed by freezing different mixtures of various hydrocarbons. There is no objection in principle to using room-temperature glasses of appropriate rigidity, but the hydrocarbon glasses formed by freezing at liquid-air temperatures offer greater flexibility and allow a greater variety of compounds to be dissolved and irradiated.

The solvents used were based on those employed in similar work by Norman and Porter,[5] one, labelled by them P.Me.H., consisting of 3 parts of *iso*pentane and 2 parts of *cyclo*hexane, and the other, labelled by them E.P.A., consisting of 5 parts of ether, 5 parts of *iso*pentane and 2 parts of ethanol. These will both form glass structures when cooled to liquid-nitrogen temperatures, and will be rigid enough to prevent recombination of the photochemically formed radicals. Care must be taken, however, to keep the specimens at this temperature, as any slight warming is often sufficient to lower the viscosity sufficiently for radical recombination to take place.

It therefore follows that one experimental condition imposed on such measurements is that the specimen should be kept at 77° K whilst it is being irradiated and also until the electron-resonance spectrum has been observed. The irradiation and electron-resonance observation can be carried out separately or simultaneously. In the first case the specimen is contained in a quartz tube, immersed in liquid nitrogen and irradiated by ultra-violet light through the sides of the quartz Dewar flask and is then transferred to the pre-cooled resonator. In the second case the specimen is placed in the cavity resonator of the spectroscope, and cooled *in situ*, and then irradiated while inside the cavity. The advantage of this method is that there is no need to move the specimen at all and the radical build-up with increasing time of radiation can be studied. It has the disadvantage, however, that it is very much more difficult to get a large light flux on to the specimen, and for this reason

the first experiments were performed with separate irradiation and then quick transfer to the cold cavity.

The resonance cavities had to be of special design in either case so as to allow quick transfer of the cold specimens, or, alternatively, maximum light flux for the irradiating beam. The basic design is similar to that of the standard low-temperature resonators[6] employed in electron resonance, but a coned central tube is incorporated in the design, as shown in Fig. 1. In this figure the specimen can be seen mounted centrally in the cylindrical cavity, which is itself cooled in the liquid nitrogen. The ultra-violet beam is shown as focussed on to the specimen, and the need for the conical tube leading out through the liquid nitrogen can be clearly seen. In this way the photochemically formed radicals can be investigated while trapped in the glass surroundings, the effectiveness of this trapping process being demonstrated by the immediate disappearance of the absorption signal once the glass is warmed to the melting point.

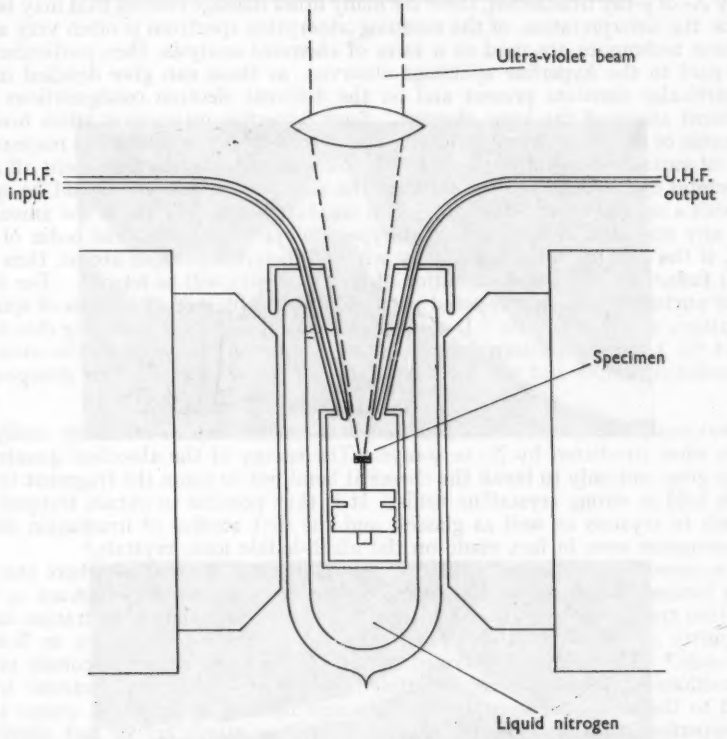


Fig. 1. Block diagram of ultra-violet irradiation experiments

The results that have been obtained so far[7] are only of a preliminary nature, but sufficient to demonstrate the wide variety of different radicals that can be formed and studied by this method. Since the existence of resolved hyperfine structure often enables an immediate identification of the chemical species to be made, this method of analysis by photochemical breakage into component parts may prove a very powerful technique. As would be expected, the wavelength of the incident radiation required to produce radicals varies from compound to compound, in some cases 366-mμ radiation is sufficient to cause decomposition, although generally 254-mμ radiation is necessary. Typical results are shown in the figures. Fig. 2 (*a*) shows the absorption obtained from a 40 per cent. solution of hydrogen peroxide and water after irradiation at 264 mμ. The shape of the line indicates unresolved hyperfine structure, which would be due to the H of the OH group. It may be noted that these radicals will

remain frozen into the glass at 90° K, but decay rapidly if kept at the temperature of solid carbon dioxide. Fig. 2 (*b*) shows the absorption obtained from a frozen solution of ethyl iodide in *iso*pentane - *cyclo*hexane mixture. The hyperfine structure in the wings is better resolved in this case, and the absorption is undoubtedly due to the ethyl radical. The last signal, shown in Fig. 2 (*c*), is that obtained from irradiated ferrioxalate solutions, and this can be obtained with 366-mμ radiation. Similar signals have also been observed from irradiated toluene, benzyl chloride and benzylamine, the benzyl radical probably being responsible for the absorption in each case.

The apparatus with which these results were obtained only incorporated crystal-video detection and the magnetic-field homogeneity was rather poor. It therefore appears that with the much greater sensitivity available by employing phase-sensitive detection, and better resolution from more homogeneous fields, much more detailed information should be available on the radical species formed. The great advantage of ultra-violet irradiation is the limit on the energy that is available for bond breakage. Although the same bonds can also be broken by X- or γ-ray irradiation, there are many other damage centres that may be produced and hence the interpretation of the resulting absorption spectrum is often very ambiguous.

If these techniques are used as a form of chemical analysis, then particular attention must be paid to the hyperfine splittings observed, as these can give detailed information on the particular elements present and on the different electron configurations concerned with different atoms of the same element. Such hyperfine interaction arises from the fact that the orbit of the unpaired electron may spend some of its time near the nuclear magnetic moments of various atoms in the radical. If, for example, the electron spent all of its time in an *s* orbital of one hydrogen atom, then the single resonance line would be split into a doublet with a separation of 500 gauss. This separation will decrease as the amount of time spent on any one atom falls and normal hyperfine splittings are of the order of 10 gauss. Similarly, if the electron interacts equally with n different hydrogen atoms, then a pattern of $(n + 1)$ lines with gaussian distribution of their intensity will be formed. For interaction with other nuclei further superimposed patterns will be obtained, a nucleus of spin I giving its own pattern of $(2I + 1)$ lines. It can be seen from this general reasoning that a complete analysis of the hyperfine pattern may give very detailed information on the atoms present in the irradiated sample and the equivalence or non-equivalence of their grouping.

High-energy irradiation chemistry

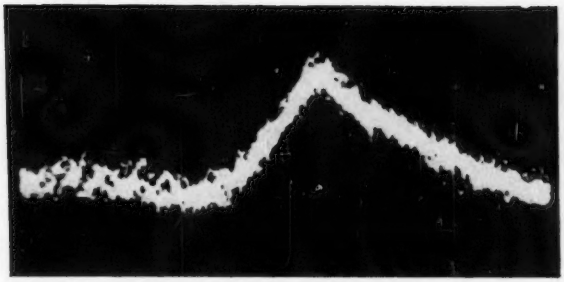
As previously mentioned, unpaired electrons can be formed relatively easily in most substances when irradiated by X- or γ-rays. The energy of the absorbed quanta are now sufficiently great not only to break the chemical bond but to cause the fragment to fly apart even when held in strong crystalline fields. It is thus possible to obtain trapped electrons and radicals in crystals as well as glasses, and the first studies of irradiation damage by electron resonance were in fact made on the alkali-halide ionic crystals.[8]

The occurrence of hyperfine structure can again be used to show where the unpaired electron is located in the crystal lattice and, as impurity atoms will often act as the most likely electron traps, this can be used in turn to measure both the concentration and nature of the impurity atoms. This is illustrated very well by the measurements on X-irradiated quartz crystals.[9] The spectrum obtained can be analysed and shown to consist of six electronic transitions each split into six hyperfine lines. The six different electronic transitions correspond to the six different equivalent positions for any atom in the quartz structure, and the hyperfine splitting indicates that the impurity atoms are in fact aluminium-27. Similar work on irradiated diamonds[10] showed that it was not only electrons that were displaced in a crystal lattice, but that the carbon atoms themselves could be displaced into interstitial positions.

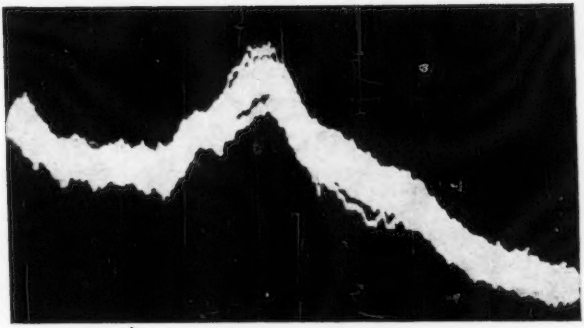
Although the initial electron-resonance work on irradiated substances was confined to inorganic compounds, a very wide field is now opening up in its application to organic chemistry.[11] In this field the specimen usually takes the form of either a powder or polycrystalline sample. Any hyperfine splitting due to electrons in p or d states will then be smeared out and only the contribution from the angular-independent *s* orbitals will be left. With most organic compounds the hyperfine structure is in fact from the hydrogen nuclei.

Hyperfine structure in chemical analysis

The detailed chemical information that can be obtained from a complete analysis of the hyperfine structure of an electron-resonance signal is best illustrated by some of the work



(*a*)



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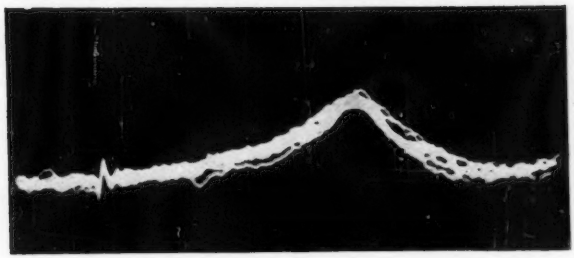

(*c*)

Fig. 2. Spectra obtained from irradiated samples: (*a*) hydrogen peroxide - glass; (*b*) ethyl iodide; (*c*) ferrioxalate

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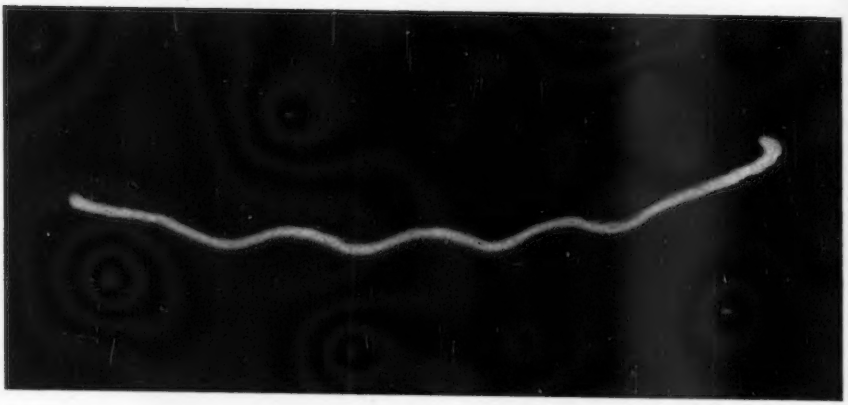
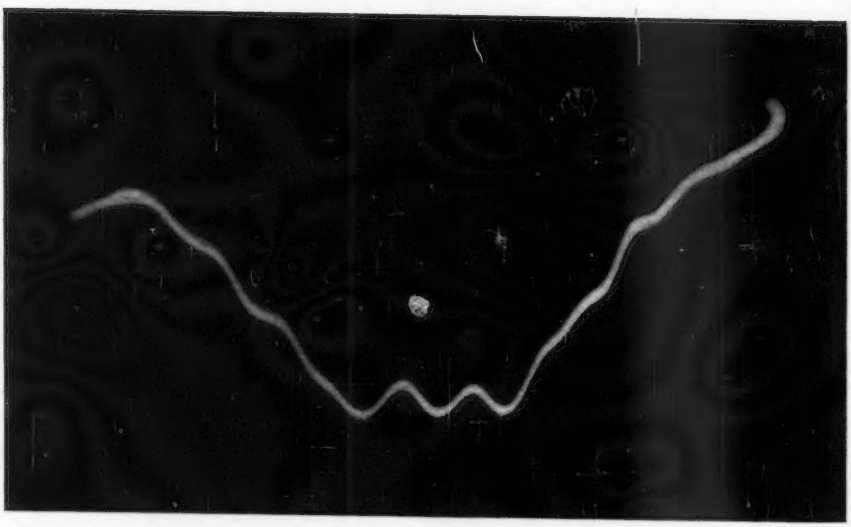


(*a*)

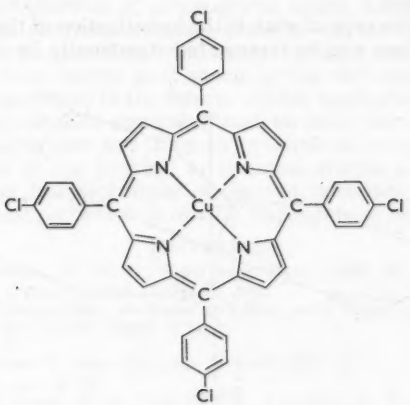


(*b*)

Fig. 3. Hyperfine structure from copper porphin derivatives: (*a*) unchlorinated derivative; (*b*) chlorinated derivative

on stable organic radicals. Thus Jarrett and Sloan[12] have found that the hyperfine splitting obtained from dimesitylmethyl can be resolved into two groups each containing thirty-five peaks. The splitting of the peaks into two groups is due to the interaction with the central hydrogen atom of the methyl group, as the unpaired electron spends much more time on the central carbon atom than on the other groups. The actual time, or more correctly the density of the electron cloud there, can in fact be calculated from the splitting between the centres of these two groups. The unpaired electron will also interact with the four *meta*-hydrogen atoms connected directly to the carbon atoms of the two phenyl groups. These would therefore be expected to produce a group of $(n + 1) = 5$ lines in each of the two sets. The fact that 35 are obtained shows that there is still a further interaction to consider. If the molecule is planar, then molecular-orbital calculations show that there will be about 400 times as much electron cloud density on the *para*-methyl groups as on the *ortho* groups of the two phenyl rings. If this is so, each of their three hydrogen atoms will also interact with the π orbital of the unpaired electron to split each line into a further $(6 + 1)$ components. The thirty-five components can thus be completely explained and, in the process, the detailed wave functions over the whole molecule can be calculated. This example is typical of the very precise information that can be obtained from free radical studies. It is clear that the distinctive variations and splittings of the spectra can be used as a sensitive means of detecting different groups in an unknown compound, and hence may prove a powerful analytical tool in certain cases.

This is not limited to hydrogen groupings either, as any atom with a nuclear moment can give rise to a hyperfine interaction. The work of Griffiths and Owen[13] on ammonium chloroiridate in which the hyperfine structure from the chlorine is found superimposed on that from the iridium permitted very detailed calculations to be made on the percentage electron transfer and π bonding present in this and other compounds. Another case of particular interest that we have recently investigated is that of chlorinated tetraphenyl copper porphin, in which a hyperfine interaction from the outer edge chlorine atoms is found superimposed on the four lines from the central copper atom. This is illustrated in Fig. 3, where the spectrum from the unchlorinated derivative is shown at the top and that from the chlorinated compound is shown underneath. The distance between the copper and chlorine atoms can be seen from the following structural formula—



It is a very interesting and somewhat surprising fact that the magnetic electron of the copper can move out to the edge chlorines, presumably via the π orbitals of the ring system.

The occurrence of distinctive hyperfine structure can also be used as a very powerful analytical tool in the more practical case of determining impurity concentrations in semiconducting material. The normally diamagnetic impurity atoms now have an odd electron or hole associated with them and thus become paramagnetic, and electron-resonance techniques can therefore not only measure their concentration but, from the number of hyperfine lines that are obtained, the impurity can be immediately identified.[14] (For example, phosphorus gives two hyperfine lines, arsenic four and antimony two groups, one set of

6 and one of 8.) This form of analysis in which the specimen is neither chemically treated nor destroyed has very promising prospects for impurity determinations.

The study of transient intermediates

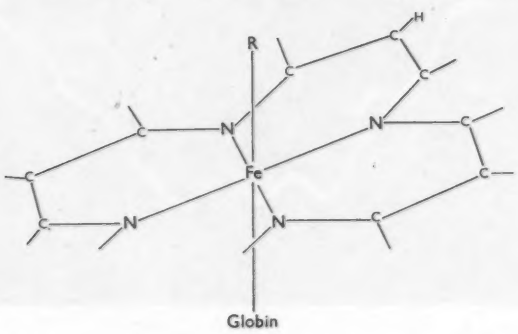
Another chemical system to which electron resonance can be applied more readily than any other technique is that of following the process of a chemical reaction in which a transient intermediate possessing an unpaired electron is formed. The growth and decay of such an intermediate can then be followed accurately by studying the growth and decay of the electron-resonance absorption signal associated with it. The characteristics of the resonance absorption itself can also be used to give information on the electronic state of the intermediate and hence on the probable mechanisms of the chemical reaction.

One series of such experiments has been conducted, namely a study of the intermediates formed on the oxidation of various phthalocyanine and porphin derivatives.[15] With each compound a strong signal was obtained, which decayed to zero as the action went through to completion, and from the width and g-value of the signal it could be established that the unpaired electron was associated with the outer ring system and that this was therefore remaining intact at this stage of oxidation. These preliminary measurements are only the beginning of a very wide field in the dynamic study of different systems.

Structural analysis

Although structural analysis is not normally classified as an analytical technique, it is worth mentioning this application of electron resonance in conjunction with the other chemical uses. Structural analysis by resonance methods depends on the fact that both the g-value and hyperfine pattern may vary with orientation if a single crystal is being studied. This angular orientation is produced by the symmetry around the paramagnetic ion and hence can be used to relate the internal symmetry of the crystal to the external crystalline axes. The great advantage of electron-resonance techniques over other methods is best seen with large organo-metallic compounds, when the mass of overlapping data obtained by infra-red spectroscopy or X-ray crystallography is exceedingly hard to interpret. Electron-resonance techniques ignore all the diamagnetic material, however, and just give a spectrum from the central paramagnetic atom, enabling detailed information to be obtained about it and its immediate surroundings.

A particular case of this type of work is the investigation of the structure of haemoglobin and its derivatives.[16] These can be represented structurally by the following figure—



It will be seen that the haem plane containing the iron atom and the four nitrogen atoms is one of the basic units. Despite very detailed work on the subject, no data on the orientation of this plane with respect to the crystal axes has yet been obtained from X-ray analysis, owing to the great complexity of the patterns observed. Electron resonance on the other hand can determine this orientation to $\pm 2°$ by simply rotating the crystal round and measuring the g-value variations. Fig. 4 indicates how the g-value will vary with angle with respect to the haem plane and hence it is only necessary to locate the direction corresponding to $g = 2{\cdot}0$ and the normal to the haem plane is determined relative to the external crystalline axes.

Many other structural details have been analysed in a similar way by electron-resonance techniques and, where applicable, it can normally give a result as accurate as that obtained from X-ray analysis, and in far less time and with much less computation.

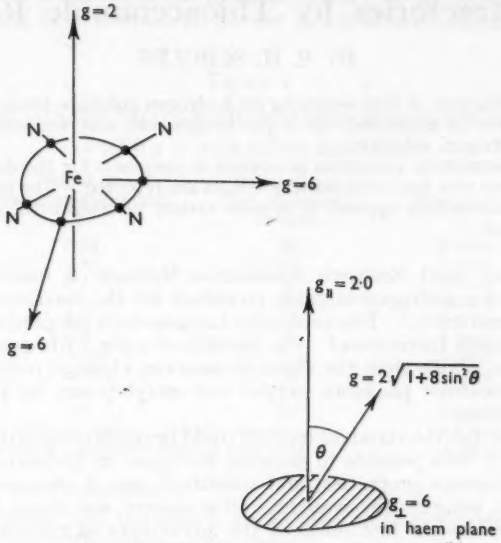


Fig. 4. Structural analysis by g-value variation

Conclusions

An attempt has been made in this paper to outline the possible applications of electron-spin resonance to different chemical problems. Apart from its obvious use as a means of measuring very small concentrations of paramagnetic atoms, it can also be applied to many systems in which unpaired electrons naturally occur or can be easily produced.

The cases of photochemical studies, irradiation chemistry and free-radical investigation have been dealt with at some length, as it would appear that more and more research will be concentrated in these directions in the future. Other applications such as the monitoring of chemical reactions and detailed structural analysis have also been mentioned, and the technique is being applied to new and different problems at an ever-increasing rate. It is probably fair to say that if any physical or chemical system possesses unpaired electron spins then, sooner or later, the techniques of electron resonance will be applied to obtain exact and detailed information, which is usually impossible to derive by any other means.

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The Determination of Iron in Iron Ores, Slags and Refractories by Thioacetamide Reduction

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The reduction of iron solutions by hydrogen sulphide formed *in situ* by the hydrolysis of thioacetamide is practicable and may successfully replace gaseous hydrogen sulphide.

A thioacetamide reduction procedure is proposed for the determination of iron in iron ores and confirmatory results are reported. The procedure has also been successfully applied to a wide variety of steelworks products and raw materials.

The British Iron and Steel Research Association Methods of Analysis Committee have recently recommended a hydrogen sulphide procedure for the determination of iron in ores, slags and refractory materials.[1] This procedure has now been adopted as a standard method by the British Standards Institution.[2] The method of using hydrogen sulphide as the sole reducing agent is less simple than the classical stannous chloride reduction method, but it overcomes interference from platinum, copper and molybdenum by precipitation of these metals as their sulphides.

It was considered that the standard method could be made more attractive for application on a routine basis if it were possible to dispense with gaseous hydrogen sulphide, in view of its corrosive and poisonous properties, and substitute one of the derivatives of thioacetic acid. Thioacetamide, being readily available in this country, was chosen for preliminary trials.

Barber and Grzeskowiak[3] first outlined the advantages of thioacetamide over gaseous hydrogen sulphide, and many workers have since used the reagent successfully for the qualitative separation of group 2 cations. The quantitative separation of antimony, arsenic, bismuth, copper, cadmium, lead, mercury, molybdenum and tin has also been fully examined and reported by Flaschka and Jakobljevich.[4] An aqueous solution of the reagent may be added directly to the solution from which the sulphides are to be precipitated; precipitation is then brought about by hydrogen sulphide, which is formed as a result of hydrolysis of the thioacetamide—

$$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S.$$

The rate of hydrolysis increases rapidly as the solution is heated and in acid solution the acetamide formed is further hydrolysed to acetic acid and ammonium ion—

$$CH_3CONH_2 + H_2O \rightarrow CH_3COOH + NH_3.$$

The time required for complete precipitation is less than that necessary with gaseous hydrogen sulphide and the low concentration of sulphide ion in solution seems to facilitate rapid coagulation and filtration of the metal sulphides.

Experimental

An initial approach was made with a sample of high-purity iron; the reduction with gaseous hydrogen sulphide described in the standard method[2] was replaced by an addition of thioacetamide dissolved in water, and the solution was then boiled for periods of 15 and 30 minutes. After removal of sulphides by filtration, 10 ml of diluted sulphuric acid (1 + 1) were added to the filtrate, which was then boiled for 30 minutes to remove excess of reagent. The solution was cooled, 5 ml of concentrated phosphoric acid were added and it was titrated with 0·1 *N* potassium dichromate, sodium diphenylaminesulphonate in preoxidised Analoid form being used as indicator.

These tests (Table I) suggested that an addition of between 0·4 and 0·5 g of thioacetamide would be sufficient and would provide an adequate excess over the theoretical amount of 0·34 g, which is required to reduce completely a solution containing 0·5 g of iron.

Reproducibility tests on samples of high-purity iron by this tentative procedure showed a marked tendency towards high results, owing to the presence of excess of thioacetamide, which produced a fading end-point during the titration. It became evident at this stage that the main drawback to the use of thioacetamide as a reducing agent in volumetric analysis

would be in the decomposition of excess of reagent before titration. In an attempt to eliminate the thioacetamide, increasing amounts of sulphuric acid were added to the filtrate and the solution was boiled for longer periods. With increasing acid concentration, the colour change at the end-point became less sharp, and consideration was given to an oxidant and an indicator that would be more suitable for use in solutions containing a high proportion of sulphuric acid.

TABLE I

PRELIMINARY TRIALS WITH THIOACETAMIDE REDUCTION

0·5000 g of high-purity iron taken

Weight of thioacetamide added, g	Boiling time for reduction, minutes	Iron found, g
0·35	15	0·4580
0·35	30	0·4640
0·4	15	0·5016
0·4	30	0·5012
0·5	15	0·5023
0·5	30	0·5016
0·75	15	0·5021
0·75	30	0·5025
1·0	15	0·5065
1·0	30	0·5043
Standard hydrogen sulphide reduction		0·4992
Standard hydrogen sulphide reduction		0·4998

CHOICE OF OXIDANT AND INDICATOR—

Ceric sulphate offers two important advantages over potassium dichromate in the titration of ferrous iron. These are as follows—

(*a*) it can be used in solutions of higher acid concentration, and
(*b*) the cerous ion is colourless and so end-point detection is much easier.

o-Phenanthroline combines in solution with ferrous salts to form an intense red tri-*o*-phenanthroline - ferrous ion (ferroin): with strong oxidising agents the pale blue ferric complex ion is formed. The colour change on addition of excess of ceric sulphate (orange-red to very pale blue) is very striking and it is much sharper than the corresponding diphenylaminesulphonate change point. An addition of 0·5 ml of 0·005 *M* ferroin indicator solution is sufficient for a titration, giving an almost negligible indicator blank of approximately 0·025 ml of 0·1 *N* ceric sulphate.

TABLE II

EFFECT OF SULPHURIC ACID CONCENTRATION ON DECOMPOSITION OF EXCESS OF THIOACETAMIDE

Volume of sulphuric acid added to filtrate, ml	Approximate normality of solution	Volume of 0·1 *N* ceric sulphate, ml
5	0·7	10·35
		10·30
12·5	1·2	10·20
		10·25
25	2·1	10·10
		10·15
37·5	3·0	10·08
		10·10
50	3·9	10·05
		10·07
60	4·7	10·03
		10·07
75	5·7	10·03
		10·05
90	6·8	10·04
		10·05

DECOMPOSITION OF EXCESS OF THIOACETAMIDE—

In order to assess the effect of increased acid concentration on the decomposition of thioacetamide, several tests were carried out, the sample being omitted, with 0·2-g additions of thioacetamide—this being the maximum amount of reagent that would be present as excess after complete reduction of iron. To each test solution were added 10·0 ml of standard 0·1 *N* ferrous ammonium sulphate together with 0·5 ml of 0·005 *M* ferroin as indicator, and the solution was titrated with 0·1 *N* ceric sulphate, with the results shown in Table II.

Hence it is necessary, after separation of sulphides, to make the filtrate about 6 *N* with respect to sulphuric acid in order to ensure complete decomposition of excess of thioacetamide.

INTERFERENCE OF VANADIUM—

Oxidation with potassium permanganate ensures that vanadium is present in the quinquivalent state before thioacetamide treatment; hydrogen sulphide reduces this to the quadrivalent condition, which may then be slowly oxidised during the titration with ceric sulphate. This results in a transient end-point. Walden, Hammett and Edmonds[5] state that this oxidation back to the quinquivalent condition may be avoided if the solution is made 5 *M* in sulphuric acid before titration. Tests with samples of pure iron to which a standard solution of vanadium was added confirm that the end-point becomes more difficult to detect with increasing vanadium content. The addition of a further 120 ml of diluted sulphuric acid (1 + 1) to give a final acid concentration of about 10 *N* before titration gives a sharp and vivid end-point, which occurs when the iron is quantitatively oxidised and the vanadium is still entirely in the quadrivalent state (Table III).

TABLE III

EFFECT OF SULPHURIC ACID CONCENTRATION ON VANADIUM INTERFERENCE

0·2500 g of high-purity iron taken

Weight of vanadium added, mg	Iron found with final acid concentration 6 *N*, g	Iron found with final acid concentration 10 *N*, g
Nil	0·2500	0·2500
	0·2497	0·2500
2·5	0·2500	0·2497
	0·2500	0·2497
5·0	0·2505	0·2500
	0·2508	0·2502
12·0	0·2508	0·2500
	0·2513	0·2497
25·0	0·2519	0·2500
	0·2524	0·2502

EFFECT OF CHROMIUM—

Chromium does not interfere directly, but if the amount of this element is large, giving a highly coloured green solution, the completion of the titration with ceric sulphate becomes difficult to judge. Visual observation of the end-point may, however, be considerably improved by increasing the volume of the ferroin addition from 0·5 ml to 1·0 or 2·0 ml.

Refractory materials containing high proportions of chromium, such as chrome-magnesite bricks, are normally decomposed by strong fuming with perchloric acid with consequent oxidation of the chromium. Thioacetamide reduces sexavalent chromium, and so it is necessary to increase the amounts of reagent specified in the recommended method. Alternatively, the chromium may be conveniently reduced by treatment with concentrated hydrochloric acid before the addition of thioacetamide.

METHOD

REAGENTS—

Diluted sulphuric acid (1 + 1)—Cautiously add 500 ml of concentrated sulphuric acid to 450 ml of water, cool and dilute to 1 litre.

Dilute sulphuric acid (1 + 19)—Cautiously add 50 ml of concentrated sulphuric acid to 100 ml of water, cool and dilute to 1 litre.

Perchloric acid, 60 per cent.

Hydrofluoric acid, 40 per cent.

Sodium hydroxide solution—A 5 per cent. w/v aqueous solution.

Thioacetamide solution—A 1 per cent. w/v aqueous solution.

Potassium permanganate solution—A 0·5 per cent. w/v aqueous solution.

Ferroin indicator solution—Dissolve 0·743 g of *o*-phenanthroline monohydrate in 250 ml of 0·005 *M* ferrous sulphate (0·348 g of ferrous sulphate, $FeSO_4.7H_2O$, in 250 ml of water).

Osmic acid solution—A 1 per cent. w/v solution.

Ferrous ammonium sulphate, 0·1 N—Standardise against 0·1 *N* potassium permanganate.

Ceric sulphate solution, 0·1 N—Dissolve 64 g of crystalline ceric ammonium sulphate, $(NH_4)_4Ce(SO_4)_4.2H_2O$, in a mixture of 500 ml of water and 60 ml of diluted sulphuric acid (1 + 1) and dilute to 1 litre in a calibrated flask. Filter through a well washed asbestos pad, discarding the first 50 ml of the filtrate.

STANDARDISATION OF CERIC SULPHATE SOLUTION—

Transfer 0·1978 g of Specpure arsenious oxide, previously dried at 150° C for 2 hours, to a 400-ml beaker. Add 20 ml of 5 per cent. w/v sodium hydroxide solution and heat gently until completely dissolved. Cool, dilute to 100 ml and add 10 ml of diluted sulphuric acid (1 + 1) followed by 2 or 3 drops of 1 per cent. w/v osmic acid solution. Add 0·5 ml of ferroin indicator and titrate with 0·1 *N* ceric sulphate to a pale blue end-point. Exactly 40 ml of 0·1 *N* ceric sulphate should be required for this titration. Repeat the standardisation with a second portion of arsenious oxide.

PROCEDURE—

Dissolve 0·5000 g of sample (Note 1) in 30 ml of concentrated hydrochloric acid. (Note 2.) Add 10 ml of diluted sulphuric acid (1 + 1) and evaporate to fumes. Cool, and re-dissolve salts by heating with 100 ml of water. (Note 3.) Oxidise by the dropwise addition of 0·5 per cent. w/v potassium permanganate until the solution is just pink, add 2 or 3 drops in excess and boil to destroy carbonaceous matter. Dilute to about 300 ml with water, place a boiling-rod in the beaker, cover with a clock-glass and heat to boiling. Add a suitable quantity of 1 per cent. w/v thioacetamide solution (Note 4) and continue to boil for 20 minutes. Remove the beaker from the hot-plate, add a little Whatman ashless floc to the solution and set it aside for 5 minutes. Filter through a paper-pulp pad into a 1-litre conical beaker, washing with dilute sulphuric acid (1 + 19) until the pad is free from iron salts. Add 120 ml of diluted sulphuric acid (1 + 1) to the filtrate, place a boiling-rod in the beaker, cover with a clock-glass and boil for 30 minutes. Cool (Note 5), dilute to about 450 ml, add 0·5 ml of ferroin indicator and titrate with 0·1 *N* ceric sulphate until one drop changes the colour of the solution from orange to a very pale blue-green. (Note 6.)

A blank should be carried out on corresponding quantities of all reagents employed, except for the thioacetamide, when 20 ml of 1 per cent. w/v solution should be used. To this solution add 10·0 ml of standard 0·1 *N* ferrous ammonium sulphate and titrate with 0·1 *N* ceric sulphate to determine the indicator blank plus reagent blank. The total blank should not exceed 0·05 ml of 0·1 *N* ceric sulphate.

1 ml of 0·1 *N* $Ce(SO_4)_2$ solution at 20° C ≡ 0·005585 g of iron.

NOTES—

1. The laboratory sample should be prepared as described in British Standard 1121:Part 33.[3] It is specially recommended that all samples of iron ore should be "air-dried," *i.e.*, exposed to the laboratory atmosphere until a stable state with respect to moisture is obtained. The moisture may then be determined concurrently with the iron by the method described in British Standard 1016[6] and the iron value obtained can be corrected to a moisture-free basis.

2. The decomposition procedures outlined in the standard method are applicable to samples that are insoluble in hydrochloric acid.

For samples having high contents of calcium, 10 ml of 60 per cent. perchloric acid should be substituted for sulphuric acid.

For chrome-magnesite refractories that have been decomposed by fuming with perchloric acid, it is necessary, before adding thioacetamide, to reduce the sexavalant chromium as follows—

Cool the fumed residue, add 10 ml of concentrated hydrochloric acid and 10 ml of water and gently evaporate to fumes, avoiding re-oxidation of the chromium. Cool slightly and dilute with water.

3. For absolute accuracy samples of iron ores and other materials containing silica should be treated as follows—

Filter the solution through a paper-pulp pad, washing with dilute sulphuric acid (1 + 19), ignite

the residue in a platinum crucible and treat with 40 per cent. hydrofluoric acid to volatilise silica. Fuse the residue with 1 g of sodium bisulphate and extract in the main solution.

4. Suitable volumes of 1 per cent. w/v thioacetamide solution are as follows—

Iron content, %	up to 20	20 to 40	40 to 60	60 to 80	80 to 100
Volume of solution required, ml	20	26	34	40	48

Difficulty in decomposing the excess of reagent may be experienced if these quantities are exceeded.

5. For samples containing more than 0·25 per cent. of vanadium, add 100 ml of diluted sulphuric acid (1 + 1) before titration.

6. For highly coloured solutions, the amount of indicator solution may be increased up to 2·0 ml.

Results

In Table IV, the results obtained on ten circulated samples of iron ore are compared with results obtained by Members of the B.I.S.R.A. Methods of Analysis Committee by the standard hydrogen sulphide method.[1] A further series of results with samples of steel-making slags, refractory materials and so on is given in Table V.

Samples of iron ore and high-purity iron have each been analysed twelve times on different occasions over a period of several months. Table VI shows good replicate analyses and together with the results presented in Tables IV and V is considered to provide satisfactory evidence of the reliability of the thioacetamide reduction method.

Table IV

Comparison between hydrogen sulphide and thioacetamide reduction methods of determining iron in iron ore

Sample	Type	Iron by hydrogen sulphide method,* %	Iron by thioacetamide method,† %
MGS 80	Kiruna	65·3	65·25
MGS 81	Cleveland ironstone	30·5	30·5
MGS 82	Djerissa	57·2	57·25
MGS 83	Sproxton	41·85	42·0
MGS 84	Lincolnshire	24·85	24·85
MGS 85	Haematite	40·05	40·05
MGS 86	May-sur-Orne	43·6	43·75
MGS 88	Wabana	52·5	52·6
B.C.S. No. 244	Magnetite	55·8	55·75
B.C.S. No. 245	Haematite	33·8	33·7

* Obtained by the B.I.S.R.A. Methods of Analysis Committee.

† Mean of 3 determinations (fourth significant figure given to nearest 0·05 per cent.).

Table V

Comparison between hydrogen sulphide and thioacetamide reduction methods of determining iron in miscellaneous samples

Sample	Type	Iron by hydrogen sulphide method,* %	Iron by thioacetamide method,† %
MGS 101	Basic slag	11·5	11·4
MGS 103	Aluminous clay	7·05	7·05
MGS 104	Manganese ore	15·0	15·05
MGS 106	Chrome-magnesite brick	8·05	8·02
MGS 107	Tap cinder	49·45	49·3
MGS 129	Bauxite	15·75	15·7
MGS 147	Basic slag	8·75	8·70
B.C.S. No. 208	Ferro-manganese alloy	13·37‡	13·35
B.C.S. No. 269	Aluminous firebrick	2·45‡	2·41

* Obtained by the B.I.S.R.A. Methods of Analysis Committee.

† Mean of 3 determinations (fourth significant figure given to nearest 0·05 per cent.).

‡ B.C.S. certificate value.

TABLE VI

REPLICATE ANALYSES OF IRON ORE AND PURE IRON

B.C.S. No. 175: *iron ore "A"* (58·08 *per cent. of iron by hydrogen sulphide method**)—
Iron found, %: 58·11, 58·03, 58·02, 58·06, 58·10, 57·97, 57·94, 57·82, 57·99, 58·04, 58·09, 57·89
Mean, %: 58·01
Standard deviation ± 0·08 per cent.

Special pure Swedish iron (99·92 *per cent. of iron by difference*)—
Iron found, %: 100·09, 99·97, 99·97, 100·05, 100·05, 99·97, 99·97, 99·86, 99·79, 99·77, 99·90, 100·00
Mean, %: 99·95
Standard deviation ± 0·10 per cent.

* Obtained by the B.I.S.R.A. Methods of Analysis Committee.

CONCLUSION

A method has been developed in which the principle of hydrogen sulphide reduction can be applied to the routine analysis of iron ores without the need for a supply of gaseous hydrogen sulphide. Laboratory staff are thereby freed from the health hazards associated with hydrogen sulphide generators. Ceric sulphate and ferroin indicator solution have been found particularly suitable as oxidant and indicator at the high acid concentrations required to remove the excess of reducing agent.

The method has been applied to a wide variety of steel-making slags, raw materials and refractories, and the results obtained are in good agreement with mean values established by the standard hydrogen sulphide method.

Thanks are due to Miss D. V. Swindell for carrying out a considerable portion of the experimental work and to Members of the B.I.S.R.A. Methods of Analysis Committee for providing analysed samples.

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Studies on Hypovanadous Salts as Analytical Reagents

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The standardisation of solutions of hypovanadous sulphate and chloride with potassium permanganate, ceric sulphate, potassium dichromate, potassium iodate and with ferric salts has been investigated: end-points were determined both visually and potentiometrically. Potassium iodate was found to be the most accurate reagent, but, for routine titrations, ferric salts are more convenient.

The determination of nitrate has been improved and the modified procedure applied to the determination of hydroxylamine. The increased reducing power of the hypovanadous ($V^{\cdot\cdot}$) ion in weakly acid, buffered solution has been utilised for the determination of difficultly reducible nitro compounds, such as 2-nitro-*m*-xylene and nitroguanidine. Azobenzene is reduced quantitatively to hydrazobenzene (which rearranges to benzidine) in 0·5 to 2 *N* hydrochloric acid solution; it can be titrated directly with hypovanadous chloride solution, phenosafranine being used as indicator.

THE hypovanadous ion, $V^{\cdot\cdot}$, is a powerful reducing agent in aqueous solution, as indicated by the standard oxidation potential at 25° C, $E°_{V^{III}/V^{II}} = -0{\cdot}255$ volt.[1] Such solutions thus

lie between titanous solutions ($E°_{Ti^{IV}/Ti^{III}} = 0{\cdot}10$ volt) and chromous solutions ($E°_{Cr^{III}/Cr^{II}} = -0{\cdot}40$ volt) in reducing power. Solutions of hypovanadous salts have not, however, been widely used in volumetric analysis and the methods of standardising them have never been compared. The solutions are inherently unstable, evolving hydrogen and decreasing in strength owing to reduction of the hydrogen ions present—

$$2V^{\cdot\cdot} + 2H^{\cdot} = 2V^{\cdot\cdot\cdot} + H_2;$$

this process is fairly slow in the absence of catalysts. In addition, hypovanadous solutions must be stored and used in an inert atmosphere, owing to the rapidity with which they react with oxygen.

Solutions have previously been prepared by reduction of acidified ammonium metavanadate, vanadyl sulphate or vanadyl chloride, either electrolytically[2,3] or with amalgamated zinc.[4,5] Titrations have been carried out potentiometrically,[2,6] amperometrically[5] and with indicators.[3,4,5,7,8,9]

In this investigation the solutions of vanadium^{II} salts were prepared in a modification of the apparatus of Lingane and Pecsok,[10] by reduction of ammonium metavanadate or vanadyl chloride. We find that the best procedure for standardisation is with potassium iodate, but titration with a standard solution of a ferric salt, with phenosafranine as indicator, is more convenient for routine work. Satisfactory results are also obtained by direct titration of potassium dichromate in 6 *N* sulphuric acid, provided that the experimental conditions given below are followed closely.

Nitrate and hydroxylamine may be determined accurately by adding excess of a standard hypovanadous solution, heating at 95° to 100° C for a few minutes, cooling to room temperature, and titrating the excess of vanadium^{II} with ferric alum, phenosafranine being used as indicator (compare Banerjee[7]).

Advantage is taken of the greater reducing power of solutions of hypovanadous salts in weakly acid, buffered solution (pH about 4·5) in the determination of otherwise difficultly reducible nitro compounds, such as 2-nitro-*m*-xylene and nitroguanidine.

Azobenzene is quantitatively reduced to hydrazobenzene by direct titration in hydrochloric acid (not less than 0·5 *N*) with hypovanadous chloride solution, phenosafranine being used as indicator.

Experimental

Apparatus—

The apparatus is shown in Fig. 1. A is a 1-litre Pyrex-glass reservoir; the lower part, B, accommodates a cylindrical filter, consisting of sections of glass tubing of 2 mm bore fused together inside a larger tube, covered with a layer of glass-wool, and forms a support for the amalgamated zinc. C is a spring-loaded B10 ground-glass joint. Tap F is connected to the 50-ml burette, E, and the delivery tube, D, by short lengths of rubber "pressure" tubing. The double burette clamp and rubber-covered ring supporting A are fixed to the metal sleeve, H, which can be secured in any position on a large retort stand, J. A has a B24 two-way ground-glass connector leading to a hydrogen generator (containing analytical-reagent grade zinc and sulphuric acid) via a trap, G: G is charged with acidified hypovanadous sulphate solution to remove traces of oxygen from the hydrogen and also acts as a guard tube when the generator is disconnected. The burette, E, is readily detached for cleaning with the aid of screw-clips on the rubber tubing; the air in it should be flushed out with nitrogen before it is replaced. Vaseline is a satisfactory lubricant for the stop-cocks.

The reservoir was half-filled with amalgamated zinc (500 g), prepared from granulated analytical-reagent grade zinc as detailed by Stone and Hume.[11] The extent of amalgamation was usually about 1 per cent. After being washed thoroughly with distilled water, the amalgamated zinc was placed in the reservoir and allowed to drain; the 500 g lasted for several months.

Titrations were carried out in 100-ml or 250-ml flat-bottomed three-necked Pyrex-glass flasks. The central neck carried a glass tube reaching to the bottom of the flask (nitrogen inlet), a thermometer, if necessary, and (for potentiometric titrations) an indicator electrode of bright platinum wire. The two side-necks of the flask carried rubber bungs, which were pierced with holes only slightly larger than the capillary extensions fitted to the jets of the burettes used. All titrations were carried out in a stream of purified cylinder nitrogen; oxygen in the gas was removed by passage through dilute acidified hypovanadous sulphate

solution, followed by distilled water. Solutions were stirred by means of the nitrogen or magnetically; the flask could be heated by an electric hot-plate.

Potentials were measured with a Tinsley potentiometer (type 3387B, reading to 0·1 mV) against a calibrated saturated-calomel electrode; the latter was connected to the solution by a salt bridge of the type described by Irving and Smith[12] and containing mineral acid of the same concentration as that in the solution being titrated.

All burettes, pipettes, flasks and weights used were carefully calibrated.

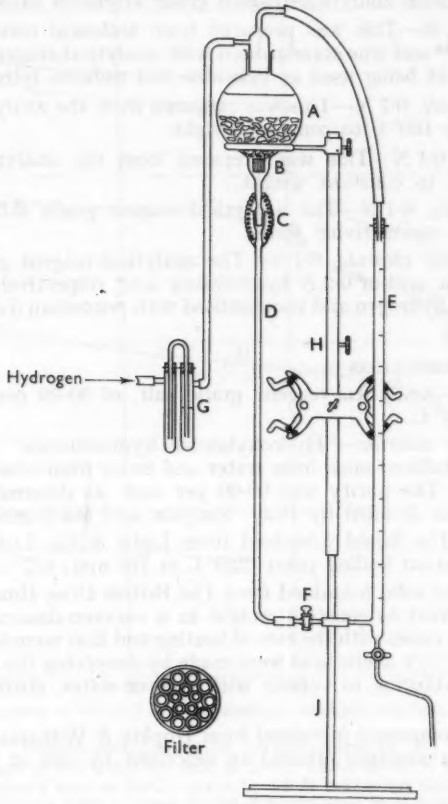

Fig. 1. Apparatus for the preparation and storage of solutions of hypovanadous salts

REAGENTS—

Vanadium solutions for reduction to the bivalent state

The solutions were 0·025 *M* to 0·1 *M* in vanadium and usually *N* in sulphuric or hydrochloric acid. They were prepared from the following salts.

Ammonium metavanadate, NH_4VO_3—The analytical-reagent grade salt was recrystallised from dilute ammonia solution (compare Lachartre[13]); the purity found by reduction with sulphur dioxide followed by titration with potassium permanganate was 100·0 per cent. The salt was dissolved in warm water, the solution was cooled, a cold dilute (1 + 5) solution of the requisite amount of sulphuric or hydrochloric acid was added, with constant stirring to prevent local precipitation of vanadium pentoxide, and the solution diluted to volume.

Vanadyl chloride solution, $VOCl_2$ aq.—The laboratory reagent solution, obtained from The British Drug Houses Ltd., nominally 50 per cent. w/v, was about 3 *M* in vanadium. It was diluted with dilute hydrochloric acid to the required concentration.

These solutions were reduced by being set aside overnight (with occasional shaking) in contact with amalgamated zinc (see Fig. 1). The hypovanadous solutions in *N* sulphuric acid were stable for about 3 weeks and in *N* hydrochloric acid for about 2 weeks. They were standardised daily.

Solutions of oxidants for standardisation of hypovanadous salt solutions

Potassium permanganate, 0·1 N—This was prepared from the analytical-reagent grade salt and standardised with analytical-reagent grade arsenious oxide.

Ceric sulphate, 0·1 N—This was prepared from technical ceric ammonium nitrate, as described by one of us,[14] and was standardised with analytical-reagent grade arsenious oxide, N-phenylanthranilic acid being used as indicator and osmium tetroxide as catalyst.

Potassium dichromate, 0·1 N—This was prepared from the analytical-reagent grade salt, after drying at 140° to 150° C to constant weight.

Potassium iodate, 0·1 N—This was prepared from the analytical-reagent grade salt, after drying at 120° C to constant weight.

Sodium thiosulphate, 0·1 N—The analytical-reagent grade salt was dissolved in the appropriate volume of conductivity water.

Ferric alum or ferric chloride, 0·1 N—The analytical-reagent grade salt was dissolved in either 0·1 *N* sulphuric acid or 0·2 *N* hydrochloric acid, respectively, prepared with boiled-out water, stored under hydrogen and standardised with potassium dichromate after reduction with stannous chloride.

COMPOUNDS FOR DETERMINATION—

Potassium nitrate—Analytical-reagent grade salt, of 99·99 per cent. purity, dried to constant weight at 110° C.

Hydroxyammonium chloride—"Hydroxylamine hydrochloride" (obtained from May & Baker Ltd.) was recrystallised once from water and twice from absolute ethanol, and dried for 1 hour at 120° C. The purity was 99·90 per cent. as determined by oxidation with saturated ferric alum, as detailed by Bray, Simpson and MacKenzie.[15]

2-*Nitro*-m-*xylene*—The liquid (obtained from Light & Co. Ltd.) was redistilled twice and the fraction of constant boiling point (220° C at 755 mm; $n_D^{20°C} = 1·5218$) was collected.

Nitroguanidine—The solid (obtained from The British Drug Houses Ltd.) was recrystallised from water and dried to constant weight in a vacuum-desiccator; m.p. 236° C, with decomposition (the m.p. varies with the rate of heating and that recorded is for rapid heating). Solutions in 10 per cent. v/v acetic acid were made by dissolving the nitroguanidine in warm glacial acetic acid and diluting to volume with air-free water, stirring constantly to avoid local precipitation.

Azobenzene—This compound (obtained from Hopkin & Williams Ltd.) was distilled and then recrystallised from absolute ethanol as described by one of us[16]; m.p. 68° C, after drying *in vacuo*.

STANDARDISATION OF SOLUTIONS OF HYPOVANADOUS SALTS—

A hypovanadous salt can yield three successive end-points upon oxidation—

(*i*) vanadous salt (green): $V^{\cdot\cdot} = V^{\cdot\cdot\cdot} + e$,
(*ii*) vanadyl salt (blue): $V^{\cdot\cdot\cdot} + H_2O = VO^{\cdot\cdot} + 2H^{\cdot} + e$,
(*iii*) vanadate (yellow): $VO^{\cdot\cdot} + 2H_2O = VO_3' + 4H^{\cdot} + e$.

End-point (*iii*) is attained with permanganate, ceric salts and dichromate, but only end-point (*ii*) with iodate and ferric salts. The use of these five oxidants for standardising was investigated thoroughly, both potentiometrically and with indicators. Titrations were carried out in a stream of purified nitrogen and solutions were always deoxygenated by passing nitrogen for 15 minutes before titration.

POTENTIOMETRIC TITRATIONS—

Addition of oxidising agents to hypovanadous solutions was generally unsatisfactory, because of the danger of the oxidation of the hypovanadous ion by hydrogen ion being catalysed by the platinum electrode—

$$V^{\cdot\cdot} + H^{\cdot} = V^{\cdot\cdot\cdot} + \tfrac{1}{2}H_2.$$

Low titres and high anomalous potentials, for which this reaction was assumed to be responsible, were observed in stage (*i*) during the titration of permanganate at 25° C and ferric salts at 100° C (compare Lingane,[17] who observed a similar effect with chromous salts). Potentiometric titration is thus best restricted to the addition of hypovanadous salt, for then the latter is oxidised before it can react with hydrogen ion. Typical titration curves (with 25 ml of oxidant) are shown in Fig. 2, in which volumes of hypovanadous sulphate solution have been corrected for slight differences between experimental concentrations to a common

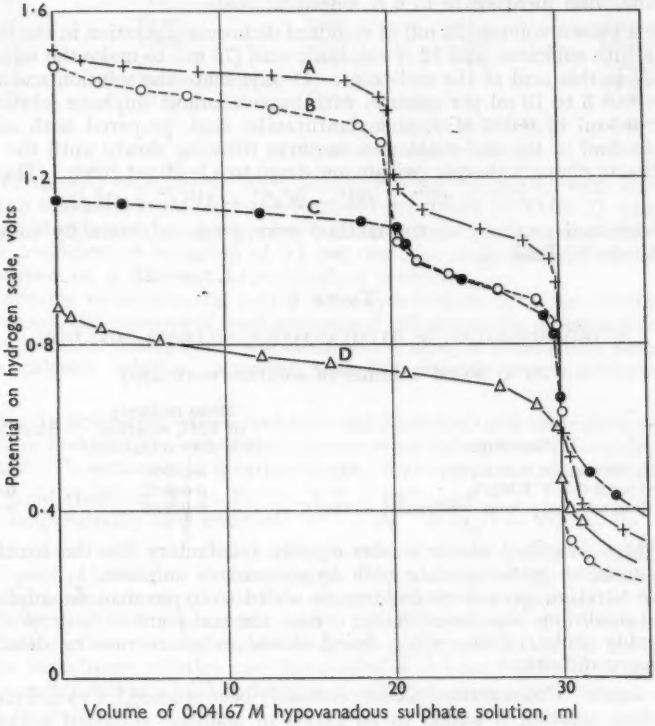

Fig. 2. Potentiometric-titration curves: curve A, 0·1 *N* potassium permanganate in 4 *N* sulphuric acid at 25°C; curve B, 0·1 *N* ceric sulphate in 2 *N* sulphuric acid at 20°C; curve C, 0·1 *N* potassium dichromate in *N* sulphuric acid at 100°C; curve D, 0·1 *N* ferric alum in *N* sulphuric acid at 100°C. In all titrations 25 ml of oxidant were used

basis of 0·04167 *M*. Permanganate (in 4 *N* sulphuric acid) and ceric sulphate (in sulphuric or hydrochloric acid) may be titrated in the cold to the first (vanadate, VO_3') end-point of Fig. 2, whereas this end-point was poor for dichromate, even at 100° C. Dichromate and ferric salts must, for accuracy, be titrated at 100° C to the end-point corresponding to formation of vanadyl ion ($VO^{\cdot\cdot}$) as found by Maass.[2] In all cases, potentials were established rather slowly near the end-points and generally 1 to 2 minutes at least elapsed before equilibrium was attained. It was found preferable to use visual rather than potentiometric methods whenever possible.

VISUAL TITRATIONS—

Potassium permanganate—Titration with permanganate in presence of sulphuric acid to the first permanent pink coloration has frequently been used for determining bivalent vanadium.[1,18,19] The reaction is slow at room temperature and is best carried out at 60° to 70° C. The reverse titration has not been reported, but it gave satisfactory results

at about 60° C provided that the permanganate was strongly acidified (4 *N* in sulphuric acid) to prevent precipitation of manganese dioxide.

Ceric sulphate—Diphenylamine (compare Banerjee[8]) was found by potentiometric titration to be subject to an indicator error of about 0·1 ml for 25 ml of 0·1 *N* ceric sulphate solution. We prefer to employ N-phenylanthranilic acid as indicator with solutions of ceric sulphate in 6 *N* sulphuric acid, and use the procedure detailed below for dichromate.

Potassium dichromate—The preferred procedure utilises N-phenylanthranilic acid with solutions of potassium dichromate in 6 *N* sulphuric acid—

Place a known volume (25 ml) of standard dichromate solution in the titration vessel and dilute with sufficient cold 12 *N* sulphuric acid (75 ml) to make the solution approximately 6 *N* in this acid at the end-point. Deoxygenate the solution and titrate slowly (no more than 5 to 10 ml per minute) with hypovanadous sulphate solution. Add the indicator (0·5 ml of 0·005 *M* N-phenylanthranilic acid, prepared with air-free water) within 1 to 2 ml of the end-point and continue titrating slowly until the violet colour of the indicator changes sharply (within one drop) to a brilliant green. The reaction is—

$$Cr_2O_7'' + 3V^{\cdot\cdot} + 8H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + 3VO^{\cdot\cdot} + 4H_2O.$$

The precision and accuracy of the method were good, as shown by comparison with other methods in Table I.

TABLE I

STANDARDISATION OF HYPOVANADOUS SULPHATE SOLUTION

20 to 30-ml volumes of solution were used

Procedure	Mean molarity of VSO_4 solution (five determinations)	Standard deviation of mean
0·1 *N* $K_2Cr_2O_7$ titrated in 6 *N* H_2SO_4	0·04907	0·00009(2)
VSO_4 titrated with 0·1 *N* $KMnO_4$	0·04901	0·00010(2)
0·1 *N* ferric alum titrated potentiometrically at 100° C ..	0·04906	0·00006(6)

The procedure described above is also equally satisfactory for the titration of ceric sulphate or ammonium metavanadate with hypovanadous sulphate.

The reverse titration (potassium dichromate added to hypovanadous sulphate solution) under the same conditions was unsatisfactory; near the end-point each drop of dichromate produced a muddy violet colour, which faded slowly to green, making determination of the end-point very difficult.

Potassium iodate—This reaction has not previously been studied for vanadium[II] solutions. The hypovanadous solution is added to an excess of acidified standard potassium iodate solution and the excess of the latter is determined by addition of potassium iodide, followed by titration of the liberated iodine—

$$5IO_3' + 15V^{\cdot\cdot} = 15VO^{\cdot\cdot} + 5I'$$
$$IO_3' + 5I' + 6H^{\cdot} = 3I_2 + 3H_2O.$$

It is clear that at least a 20 per cent. excess of potassium iodate solution is required, owing to the immediate reaction of the iodide formed with the potassium iodate.

The recommended procedure is as follows—

Displace the air from the flask with purified nitrogen during 5 to 10 minutes, add a known volume of air-free standard potassium iodate solution (in at least 20 per cent. excess of that required for reaction) and dilute air-free sulphuric acid (100 ml; 0·5 to 1 *N*). Stop the nitrogen flow, immediately add a known volume of the hypovanadous salt solution rapidly to the flask, stopper the latter and after 30 seconds (to allow for the completion of reaction) add an excess (2 g) of iodate-free analytical-reagent grade potassium iodide. Dilute the solution to about 200 ml with air-free water and titrate the liberated iodine with sodium thiosulphate solution (previously standardised against the iodate solution), using freshly prepared starch solution. Table II gives typical results at various acidities.

TABLE II

STANDARDISATION OF HYPOVANADOUS SULPHATE SOLUTION AGAINST POTASSIUM IODATE

Volume of 0·1000 *N* potassium iodate used, ml	Volume of hypovanadous sulphate taken, ml	Volume of 0·1007 *N* sodium thiosulphate used, ml	Acidity (H_2SO_4), *N*	Molarity of hypovanadous sulphate solution
29·97	19·99	10·04	0·1	0·04969
25·17	19·98	5·23	0·5	0·04980
30·12	19·98	10·17	0·5	0·04975
30·01	20·00	10·02	1	0·04980
29·98	19·99	10·00	2	0·04980
			Mean normality	0·04977
			Standard deviation of mean	0·00004(9)

The results showed consistently high accuracy when compared with standardisations by means of the other oxidants (*e.g.*, the solution mentioned in Table II was found to be 0·04980 *M* when standardised against potassium dichromate). The precision was excellent, as shown by a coefficient of variation of 0·1 per cent. for three sets of five determinations, each set performed on a different hypovanadous solution.

It is undesirable to acidify the iodate with hydrochloric acid, as chlorine is evolved. For the same reason, the presence of large amounts of chloride in the solution must be avoided. The procedure described above (with use of sulphuric acid) is satisfactory for standardising hypovanadous chloride solution, provided that the chloride-ion concentration does not exceed 0·2 *N*.

Ferric salts—In agreement with Gapchenko and Sheintsis,[4] and contrary to the experience of Banerjee,[3,9] we find that the use of thiocyanate as an indicator at laboratory temperature is unsatisfactory. Potentiometric titration showed that two reactions are involved, *viz.*—

(*a*) a rapid reaction: $V^{\cdot\cdot} + Fe^{\cdot\cdot\cdot} = V^{\cdot\cdot\cdot} + Fe^{\cdot\cdot}$, and
(*b*) a comparatively slow reaction: $V^{\cdot\cdot\cdot} + Fe^{\cdot\cdot\cdot} + H_2O = VO^{\cdot\cdot} + Fe^{\cdot\cdot} + 2H^{\cdot}$,

which causes the titres with both visual and potentiometric end-points to be high and erratic with a normal speed of titration. At slow speeds of titration (allowing 2 to 3 minutes between each drop added from at least 1 ml before the end-point), the titres are accurate to about 0·5 per cent. We find that phenosafranine (compare Gapchenko and Sheintsis[4]) functions well as an indicator at the end of the above reaction (*a*), provided that the ferric salt solution is added to the vanadium^{II} solution and the acidity is at least 0·5 *N*. The reverse addition (hypovanadous salt solution added to ferric salt solution) gives erratic titres. Some results are presented in Table III.

TABLE III

TITRATION OF HYPOVANADOUS SULPHATE WITH FERRIC ALUM, WITH PHENOSAFRANINE AS INDICATOR, AT DIFFERENT ACIDITIES

Three drops of 0·2 per cent. phenosafranine solution were used as indicator; 20 ml of sulphuric acid (of various concentrations) were present in solution

Volume of hypovanadous sulphate solution, ml	Volume of 0·1061 *N* ferric alum, ml	Acidity at end-point, *N*	Molarity of hypovanadous sulphate solution
20·01	18·65	0·5	0·09890
20·05	18·67	1	0·09879
20·01	18·61	2	0·09867
19·93	18·57	3	0·09883
		Mean molarity	0·09880
		Standard deviation of mean	0·00009(6)

No indicator error occurs with 2 to 3 drops of 0·2 per cent. phenosafranine solution (prepared from The British Drug Houses "adsorption indicator") and titration of chloride

solutions is equally satisfactory. The vanadium^{II} solution mentioned in Table II when standardised against potassium iodate solution was found to be 0·09888 *M*.

Determinations with solutions of hypovanadous salts

Nitrate and hydroxylamine—

Nitrate—Banerjee[7] determined nitrate by reduction to ammonia with excess of hypovanadous ammonium sulphate solution; the excess of reagent was titrated with potassium permanganate solution. We find that more satisfactory and consistent results are obtained by using a standard solution of a ferric salt to determine the excess of vanadium^{II} solution. The recommended procedure is as follows—

> Place a known volume (say, 25 ml) of potassium nitrate solution (approximately 0·01 *M*) in the titration flask and add sufficient 5 *N* sulphuric acid to render the solution 1 to 2 *N* in this acid. Deoxygenate the solution with a stream of purified nitrogen (which is continued during titration) and heat to 60° to 70° C. Add a known volume (excess) of hypovanadous sulphate solution (approximately 0·1 *M*), heat to 95° to 100° C and maintain this temperature for 2 to 3 minutes. Cool to room temperature, add two drops of 0·2 per cent. aqueous phenosafranine solution and titrate the excess of vanadium^{II} ion with standard ferric alum solution to the first red coloration. Perform a blank determination under identical conditions. The reactions involved are—
>
> $$NO_3' + 8V^{\cdot\cdot} + 10H^{\cdot} = NH_4^{\cdot} + 8V^{\cdot\cdot\cdot} + 3H_2O$$
> $$V^{\cdot\cdot} + Fe^{\cdot\cdot\cdot} = V^{\cdot\cdot\cdot} + Fe^{\cdot\cdot} \text{ (back-titration).}$$

It is important that the concentrations of both hypovanadous and hydrogen ions present be in excess of those required by the above equation.

With the use of 25·06 mg of potassium nitrate and an excess of vanadium^{II} solution of from 6 to 65 per cent., a mean result of 25·08 mg of potassium nitrate found (five determinations) with a standard deviation of 0·05 mg was obtained. Increasing the heating time to 10 minutes, the excess of vanadium^{II} to 200 per cent. and the acid concentration to 3 *N* were without effect. With smaller quantities of nitrate (5 to 10 mg) the precision may be increased by using more dilute reagents (approximately 0·03 *M*) in order to increase the volumes used, but it is then necessary to make the solution at least *N* in acid and to increase the excess of hypovanadous solution to at least 25 per cent. to attain complete reduction within 5 minutes, heating at 100° C. The presence of chloride is without effect.

Hydroxylamine—The quantitative reduction of hydroxylamine by hypovanadous ion has not been investigated previously. Reduction of hydroxyammonium salts proceeds rapidly at temperatures above 60° to 70° C—

$$NH_2OH + 2V^{\cdot\cdot} + 3H^{\cdot} = NH_4^{\cdot} + 2V^{\cdot\cdot\cdot} + H_2O.$$

Excess of hypovanadous salt must be employed. The experimental details are similar to those given above for the determination of nitrate; the reaction mixture must, however, be kept at 95° to 100° C for at least 5 minutes before cooling and titrating with standard ferric alum solution. Typical results were: 30·60 mg of pure hydroxyammonium chloride taken (in 0·05 *M* solution), and hypovanadous sulphate solution in *N* sulphuric acid used; found 30·61 mg (mean of four determinations) with a standard deviation of 0·08 mg.

It was found that varying the excess of hypovanadous solution from 10 to 250 per cent. and the heating time from 5 to 15 minutes gave identical results. The procedure was equally satisfactory with hypovanadous chloride solution in *N* hydrochloric acid.

Nitro compounds—

We find, in general agreement with Gapchenko and Sheintsis,[4] that easily reducible nitro compounds, such as nitrophenols and nitroanilines, may be determined by adding an excess of hypovanadous sulphate solution (at least 50 per cent. over the stoicheiometric quantity—

$$-NO_2 + 6V^{\cdot\cdot} + 6H^{\cdot} \rightarrow -NH_2 + 6V^{\cdot\cdot\cdot} + 2H_2O)$$

to a solution of the nitro compound in air-free *N* sulphuric acid or acetone and titrating the excess of vanadium^{II} salt, after standing for at least 5 minutes at room temperature, with standard ferric alum solution and phenosafranine as indicator. Nitro compounds that are reduced with difficulty by titanous salts, *e.g.*, 2-nitro-*m*-xylene (compare Newton, Stubbs

and Hinshelwood[20]) and nitroguanidine (compare Kouba, Kicklighter and Becker[21]; Zimmermann and Lieber[22]; Sternglanz, Thompson and Savell[23]) cannot be determined by the above-described procedure with vanadium^{II} salts, although over 90 per cent. reduction occurs upon prolonged boiling. By conducting the reduction in an acetate buffer medium (pH 4·5), moderately satisfactory results are obtained with such nitro compounds. It would appear that the reducing power of a hypovanadous salt solution is increased in weakly acid, buffered solution. Experimental details for the reduction of two difficultly reducible nitro compounds follow.

2-Nitro-m-*xylene*—Place 10 ml of 2·5 *M* sodium acetate solution and 1 ml of glacial acetic acid in the titration flask. Deoxygenate with a stream of purified nitrogen (which is continued during the titration) for 10 minutes. Add a known volume (*e.g.*, 10 ml) of 2-nitro-*m*-xylene in air-free ethanol solution (approximately 0·01 to 0·02 *M*) and then a measured volume (about 100 per cent. excess, *e.g.*, 25 ml) of hypovanadous sulphate solution (approximately 0·1 *N*). Set aside for 5 minutes, then add 10 ml of air-free 6 *N* sulphuric acid (to give a total acidity of 0·5 to 1 *N*, at which concentration the indicator is most effective) and two drops of 0·2 per cent. aqueous phenosafranine solution, and titrate the excess of vanadium^{II} salt with standard air-free ferric alum solution (approximately 0·1 *N*). Perform a blank determination under identical conditions, and keep the solutions well stirred throughout (*e.g.*, magnetically). Some typical results are presented in Table IV.

TABLE IV

REDUCTION OF 2-NITRO-*m*-XYLENE IN BUFFERED SOLUTION

1 ml of 0·1 *N* hypovanadous solution ≡ 2·519 mg of $C_8H_9NO_2$

Volume of hypovanadous sulphate solution, ml	Normality of hypovanadous sulphate solution	Volume of 0·1010 *N* ferric alum solution, ml	2-Nitro-*m*-xylene Taken, mg	Found, mg	Found, %
13·48	0·09679*	7·45	13·87	13·94	100·5
13·97		6·58	17·27	17·31	100·3
14·96	0·09829*	7·74	17·27	17·33	100·4
19·96		8·85	26·83	26·90	100·3
29·92		15·49	34·56	34·69	100·3
			Mean percentage found		100·3(6)
			Standard deviation of mean		0·1(4)

* These were different solutions. Each was standardised with the ferric alum solution.

The results are clearly consistent but always slightly high. This is probably due to the oxidation of some hypovanadous ion by hydrogen ion; the oxidation appears to be induced by the simultaneous reactions occurring in the reduction of the nitro compound, because in the absence of the latter a negligible amount of oxidation occurs under the experimental conditions. The results are sufficiently precise, however, to warrant the application of an empirical correction factor (0·9964).

Nitroguanidine—Place 10 ml of 2·5 *M* sodium acetate solution and 1 ml of glacial acetic acid in the titration flask. Deoxygenate with a stream of purified nitrogen (which is continued during the titration). Add a measured volume (excess) of hypovanadous sulphate solution (approximately 0·1 *N*) and then a known volume of nitroguanidine (*e.g.*, 25 ml) in air-free 10 per cent. acetic acid solution (approximately 0·01 to 0·02 *M*), delivered beneath the surface of the solution. Allow 1 minute for the completion of the reaction, then add 20 ml of air-free 6 *N* sulphuric acid and two drops of 0·2 per cent. aqueous phenosafranine solution, and rapidly titrate the excess of vanadium^{II} solution with standard air-free ferric alum solution (approximately 0·1 *N*). Carry out a blank determination under identical conditions and stir the solutions rapidly throughout (*e.g.*, magnetically).

$$(H_2N)_2C{=}N{\cdot}NO_2 + 6V^{\cdot\cdot} + 6H^{\cdot} = (H_2N)_2C{=}N{\cdot}NH_2 + 6V^{\cdot\cdot\cdot} + 2H_2O.$$

Some typical results are collected in Table V.

The slightly high results under the experimental conditions specified may be due either to attack of aminoguanidine by the hypovanadous ion or, more probably, to oxidation of the hypovanadous ion by hydrogen ion, induced during the reduction of the nitroguanidine. The consistency of the results appears to justify the use of an empirical correction factor (0·9941).

TABLE V

REDUCTION OF NITROGUANIDINE IN BUFFERED SOLUTION

1 ml of 0·1 *N* hypovanadous solution ≡ 1·735 mg of nitroguanidine

Volume of 0·09780 *N* hypovanadous sulphate solution, ml	Excess of hypovanadous sulphate solution, %	Volume of 0·1061 *N* ferric alum solution, ml	Nitroguanidine		
			Taken, mg	Found, mg	Found, %
9·98	1·5	0·14	16·54	16·68	100·8
14·97	50	4·76	16·54	16·64	100·6
14·98	50	4·76	16·54	16·66	100·7
19·99	100	9·43	16·54	16·55	100·1
24·81	150	13·81	16·54	16·68	100·8
29·92	20	4·96	41·44	41·63	100·5
34·94	40	9·56	41·44	41·68	100·6
				Mean percentage found	100·5(9)
				Standard deviation of mean	0·2(4)

When the procedure used for 2-nitro-*m*-xylene (addition of reagent to nitro compound) was applied to nitroguanidine, the mean percentage reduction was only 98·5 with a standard deviation of the mean of 0·4, despite reaction times of up to 15 minutes. Similar results were obtained by Sternglanz, Thompson and Savell,[23] who determined nitroguanidine in a citrate buffer solution by adding an excess of titanous chloride. The low results may be due to the formation of a very difficultly reducible compound (possibly hydrazodicarbonamidine) by interaction of nitrosoguanidine (intermediately formed) and aminoguanidine.

AZOBENZENE—

Preliminary tests with pure azobenzene indicated that in weakly acid solution (pH 4 to 5) reduction with hypovanadous sulphate led to a mixture of aniline and hydrazobenzene (the latter was isolated as benzidine sulphate); with more strongly acid solution (say 2 to 3 *N* acid), an almost quantitative yield of benzidine sulphate was obtained. Difficulties arise when an indicator (*e.g.*, phenosafranine) is employed, owing to adsorption on the precipitated benzidine sulphate: we therefore prefer to use hypovanadous chloride and thus maintain a homogeneous reaction medium. The recommended procedure follows.

Place a weighed amount (0·1 to 0·3 g) of azobenzene in the titration flask and dissolve it in a small volume of air-free ethanol (5 to 10 ml per 0·1 g of azobenzene). Displace the air from the flask with nitrogen, then add sufficient air-free concentrated hydrochloric acid (5 ml) dropwise, with shaking, to ensure that the concentration of this acid is 0·5 to 2 *N* at the end-point. Add standard hypovanadous chloride solution (approximately 0·1 *N*) slowly; shake vigorously or stir magnetically during the titration. When the yellow colour has almost faded, add two drops of 0·2 per cent. aqueous phenosafranine solution and continue the titration slowly until the colour of the solution changes from red-violet to apple-green.

$$C_6H_5N{=}NC_6H_5 + 2V^{\cdot\cdot} + 2H^{\cdot} = C_6H_5NH{\cdot}NHC_6H_5 + 2V^{\cdot\cdot\cdot}.$$

Some typical results are given in Table VI.

TABLE VI

DETERMINATION OF AZOBENZENE

1 ml of 0·1 *N* hypovanadous solution ≡ 9·111 mg of azobenzene

Titre of hypovanadous chloride solution, ml	Normality of hypovanadous chloride solution	Hydrochloric acid concentration, *N*	Azobenzene		
			Taken, mg	Found, mg	Found, %
10·03	0·09345	0·5	85·59	84·50	99·8
26·89	0·09345	1·0	227·9	229·0	100·5
22·47	0·09236	1·0	189·2	189·1	100·0
32·28	0·09236	1·0	271·2	271·6	100·2
17·21	0·09236	1·5	144·2	144·8	100·4
10·01	0·09345	2·0	85·59	85·23	99·6
10·02	0·09345	2·0	85·59	85·31	99·7
				Mean	100·0(3)
				Standard deviation of mean	0·3(5)

The work described in this paper forms part of a thesis submitted by one of us for the M.Sc. degree of the University of London. Our thanks are due to Imperial Chemical Industries Ltd. for a grant.

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Turbidimetric Determination of Chlorine in Titanium

By H. J. G. Challis and J. T. Jones

A turbidimetric procedure has been developed for the determination of chlorine in titanium. The method, based on solution of the sample in sulphuric acid and turbidimetric determination as silver chloride with a Spekker absorptiometer, is simple, rapid and more readily applicable to routine control than the standard gravimetric method. Batches of ten samples can be analysed in about 3 hours—a considerable saving in time.

Satisfactory recoveries have been obtained from solutions containing sodium chloride and titanium salts, whilst results obtained on various samples compared favourably with those of gravimetric determinations. The proposed method includes precautions necessary to overcome the heterogeneous nature of titanium sponge.

Raw titanium produced by reduction of titanium tetrachloride is liable to contain small amounts of chlorine present as chloride. The methods[1,2,3,4] recommended for the determination of this impurity are based on solution in dilute sulphuric acid and precipitation as silver chloride, but they are not readily applicable for control purposes, as long settling periods, up to 48 hours, are involved. Appreciable saving in time would be effected, therefore, if the colloidal suspension of silver chloride could be determined turbidimetrically in the presence of titanium.

This paper describes the development and evaluation of a method based on these principles, a photo-electric instrument such as a Spekker absorptiometer being used.

Experimental

Measurement of silver chloride turbidity—

Experiments were first carried out on a series of solutions containing 0·1 to 0·8 mg of chlorine (as sodium chloride) in absence and presence of titanium (0·2 g), present as sulphates.

The solutions containing titanium were oxidised with a minimum amount of nitric acid and, after addition of 5 ml of 0·5 per cent. w/v silver nitrate solution, the relationship between chlorine content and the apparent optical density of all solutions was evaluated by means of a Spekker absorptiometer (H760). Tests with various filters indicated that Ilford No. 602 was the most suitable and, using a 4-cm cell and tungsten lamp, it was established that the calibration curve, prepared as described on p. 707, was almost linear up to a concentration of 0·0006 g of chlorine per 100 ml. With higher concentrations, however, some coagulation of silver chloride occurred, and attempts to overcome this effect by addition of gum arabic produced erratic results and reduced sensitivity. Accordingly, in all other experiments, it was arranged that the chloride content of the solution did not exceed 0·0006 g of chlorine per 100 ml of solution and, under these conditions, the Spekker absorptiometer readings did not exceed 0·7.

Development of maximum intensity was next investigated on a further series of solutions containing the equivalent of 0·0004 g of chlorine in the absence of titanium and with the sulphuric acid content ranging from 0 to 10 per cent. v/v. After the addition of 5 ml of 0·5 per cent. w/v silver nitrate solution, the Spekker absorptiometer readings recorded after various time intervals were as detailed in Table I.

TABLE I

EFFECT OF TIME AND ACID CONCENTRATION ON TURBIDITY

Sulphuric acid present, % v/v	Absorptiometer readings after—		
	15 minutes	30 minutes	3 hours
Nil	0·185	0·245	0·52
1·0	0·515	0·535	0·375 (precipitated)
3·0	0·50	0·525	0·43 (precipitated)
5·0	0·51	0·525	0·48
10·0	0·485	0·52	0·51

Readings taken 15 minutes after addition of silver nitrate did not vary appreciably with acid contents between 1 and 10 per cent.; those after 30 minutes were slightly higher but again over the 1 to 10 per cent. acidity range were consistent. After 3 hours, however, precipitation of silver chloride had occurred at acid concentrations less than 5 per cent.

Further experiments established that 5 per cent. of acid was, in fact, necessary to obviate any possibility of hydrolysis of titanium salts. Accordingly, in subsequent experiments, the final acidity was controlled between 5 and 10 per cent. v/v and the readings were taken 15 to 30 minutes after addition of the silver nitrate.

TABLE II

EXPERIMENTS ON SOLUTION OF SAMPLES IN BEAKERS

Titanium present, g	Chlorine added, g	Time of solution, hours	Solution conditions	Chlorine recovered, g
Turbidimetric method—				
1·0	0·0020	2	Boiling gently	0·0014
1·0	0·0020	1½ to 2	Below boiling	0·0019
1·0	0·0020	1½ to 2	Below boiling	0·0019
1·0	0·0020	2	96° C	0·0020
1·0	0·0020	1½ to 2	Below boiling	0·0018
1·0	0·0010	1½ to 2	Below boiling	0·0008
1·0	0·0010	1½ to 2	Below boiling	0·0012
Gravimetric method—				
Nil	0·0250	3	Below boiling	0·0245
5·0	0·0250	3	Below boiling	0·0221
5·0	0·0250	3	Boiling	0·0243
5·0	0·0100	2	Below boiling	0·0078

SOLUTION OF TITANIUM IN SULPHURIC ACID—

Sulphuric acid[1] and hydrofluoric acid[4] have been recommended as solvents for titanium. Initial experiments were concerned with the use of sulphuric acid, and it was confirmed that titanium dissolved readily in diluted sulphuric acid (1 + 4) and furthermore the acid to

sample ratio was not important between 75 and 225 ml of diluted sulphuric acid (1 + 4) per g of titanium, the former volume being that recommended in a published gravimetric method.[1]

These conditions were therefore used in the preparation of solutions by dissolving, in beakers, either 1-g samples of titanium (chlorine free), with 0·0010 to 0·0020 g of chlorine (as sodium chloride) in 75 ml of diluted sulphuric acid (1 + 4) or 5-g samples and 0·0100 to 0·0250 g of chlorine in 375 ml of diluted sulphuric acid (1 + 4). Solution of the titanium was completed by heating just below the boiling point and, after oxidation with nitric acid, the chlorine content was determined either by the proposed turbidimetric procedure on the 1-g samples or gravimetrically on the 5-g samples. The results of these experiments are tabulated in Table II and indicate that, under the conditions defined, there is a possibility of loss of chlorine. A further disadvantage was that, during solution of the samples, frequent attention was necessary to avoid boiling and to correct for evaporation.

In the next series of experiments solutions were prepared by dissolving the titanium samples under reflux, the chlorine content being again determined by either the turbidimetric or gravimetric procedures. The results obtained are tabulated in Table III.

TABLE III

EXPERIMENTS ON SOLUTIONS OF SAMPLES UNDER REFLUX

Titanium present, g	Chlorine added, g	Time of solution, hours	Solution conditions	Chlorine recovered, g
Turbidimetric method—				
1·0	0·0001	1	Boiling	0·0001
1·0	0·0005	1	Boiling	0·0005
1·0	0·0010	1	Boiling	0·00095
1·0	0·0015	1	Boiling	0·0015
1·0	0·0030	1	Boiling	0·0030, 0·0030
1·0	0·0045	1	Boiling	0·0045
1·0	0·0075	1	Boiling	0·0075
Gravimetric method—				
5·0	0·0025	2	Boiling	0·00235
5·0	0·0075	2	Boiling	0·0071
5·0	0·0150	2	Boiling	0·0154
5·0	0·0300	2	Boiling	0·0299

By dissolving samples under reflux, the time of solution was reduced, and as boiling was permissible, less attention was necessary; furthermore, the recovery of chlorine was more consistent than in the previous experiments, particularly with 1-g samples.

SOLUTION OF TITANIUM IN HYDROFLUORIC ACID—

Titanium can be dissolved in hydrofluoric acid in either plastic or platinum dishes but, before transferring the solution to glassware, boric acid must be added to convert the excess of hydrofluoric acid to fluoroboric acid.[4] Some comparative results are detailed in Table IV for 1-g samples of granules dissolved either in hydrofluoric or sulphuric acid, the chlorine content being determined turbidimetrically.

TABLE IV

COMPARISON OF SOLUTION IN SULPHURIC OR HYDROFLUORIC ACID: TURBIDIMETRIC METHOD

Sample mark	Chlorine found: solutions in diluted sulphuric acid (1 + 4) under reflux, %	Chlorine found: solution in hydrofluoric acid, %
A	0·14	0·15
B	0·18	0·17
C	0·16	0·17
D	0·38	0·32
E	0·12	0·14
F	0·13	0·12

These results indicate that similar figures can be obtained by the turbidimetric method when samples are dissolved in either solvent. Solution in hydrofluoric acid has the advantage of speed; a 1-g sample can be dissolved in about 20 minutes compared with 1 hour under reflux with diluted sulphuric acid (1 + 4)—also solution can be effected without heating, thereby eliminating the possibility of loss of chlorine by volatilisation. These advantages are outweighed, however, by the expense of platinum ware, the restriction of sample weight when either platinum or plastic is used, the higher and sometimes variable blank of 0·01 to 0·02 per cent., and also the hazards involved in the use of hydrofluoric acid. Except when speed is the prime consideration, solution in sulphuric acid under reflux is to be preferred.

COMPARISON OF GRAVIMETRIC AND TURBIDIMETRIC METHODS—

The gravimetric method,[1] as well as the turbidimetric method described on p. 707, were next employed for the determination of chlorine in numerous samples of titanium sponge, granules and ingots, and the results obtained are compared in Table V.

TABLE V

COMPARISON OF GRAVIMETRIC AND TURBIDIMETRIC METHODS

Sample type	Sample No.	Chlorine by gravimetric method, %	Chlorine by turbidimetric method, %
Titanium sponge (separate sample for each determination)	1	0·10, 0·12	0·085
	2	0·16	0·175
	3	0·14, 0·15	0·15
	4	0·26, 0·40	0·27
	5	0·15, 0·15	0·17
	6	0·14	0·20
	7	0·11	0·09
Titanium sponge (aliquots from same bulk solution)	8	0·03	0·04, 0·04
	9	0·11	0·09, 0·09
	10	0·08	0·09
	11	0·09	0·10
	12	0·145	0·15
	13	0·14	0·13
	14	0·17	0·17
	15	0·17	0·16
	16	0·20	0·21
	17	0·23	0·23
	18	0·12	0·14, 0·15
	19	0·13	0·14, 0·15
Titanium granules (separate samples)	20	0·17	0·18
	21	0·33	0·32, 0·29
	22	0·34	0·28, 0·32
	23	0·29	0·29, 0·29
	24	0·36	0·36, 0·36
	25	0·25	0·28, 0·27
	26	0·28	0·31, 0·31
	27	0·30	0·33, 0·32
Titanium ingots (separate samples)	28	0·004	0·003
	29	0·005	0·005

It will be seen that the first set of comparative results obtained on separate samples of titanium sponge were inconsistent owing, it was suspected, to the heterogeneous nature of the material. Accordingly, bulk solutions of 10 g or more were prepared and when both procedures were applied to aliquot portions, concordant results were obtained over the range tested. In contrast, the results obtained on the more homogeneous titanium granules and ingots were quite acceptable for control purposes.

Although a relatively large weight is advocated in the assay of titanium sponge, it should be emphasised that extreme care must still be exercised in sampling, because of segregation in this type of raw material. Experience has shown that the bulk should be sampled preferably by riffling down to a 1-lb sample, followed by compacting and drilling to obtain a representative 10-g sample. Titanium granules should also be sampled systematically, but, in contrast, a 1-g sample is normally sufficient, owing to the finer state of division.

METHOD FOR THE TURBIDIMETRIC DETERMINATION OF CHLORINE IN TITANIUM

SAMPLING—

Titanium sponge—Riffle the consignment down to about 450 g and compact under a pressure of about 25 tons per square inch to a block about 2 inches × 2 inches × 1½ inches. Drill at least nine evenly spaced ⅜-inch holes through the entire block; this will provide about 50 g of material.

Mix the drillings thoroughly, weigh, sieve (No. 44 B.S. sieve) and weigh the separate fractions. All samples for analysis must comprise coarse and fine drillings in proportion to the weight of these two fractions.

Alternatively, if compacting facilities are not available, riffle the consignment down to about 450 g, and then cone and quarter to provide a sample weight of about 10 g.

Titanium granules—Obtain about 450 g from the consignment by riffling, or coning and quartering.

Titanium ingots or wrought products—After removal of surface oxide skin, sample by drilling or machining.

REAGENTS—

Sulphuric - nitric acid mixture—To 80 ml of water add 20 ml of nitric acid, sp.gr. 1·42. Cool to room temperature and add cautiously 100 ml of sulphuric acid, sp.gr. 1·84. Cool as before.

Standard chlorine solution—Dissolve 0·412 g of sodium chloride (dried at 110° C) in water and dilute to 1 litre. Dilute 100 ml of this solution to 250 ml.

1 ml ≡ 0·1 mg of chlorine.

Titanium sulphate solution—Dissolve 2 g of chlorine-free titanium in 150 ml of diluted sulphuric acid (1 + 4): warm gently to assist solution and then oxidise with a slight excess of nitric acid, sp.gr. 1·42. Heat the solution just to its boiling point, then cool it, and filter it if necessary through a Whatman No. 40 filter-paper, into a 200-ml calibrated flask and dilute to the mark.

PROCEDURE FOR PREPARATION OF CALIBRATION GRAPH—

Transfer 20-ml portions of the chlorine-free titanium solution to seven 100-ml calibrated flasks and add separately 1·0, 2·0, 3·0, 4·0, 5·0 and 6·0 ml of the standard chlorine solution (1 ml ≡ 0·1 mg of chlorine); use the remaining solution as a blank. Proceed with each solution as follows—

> Add 10 ml of the sulphuric - nitric acid mixture and dilute to about 80 ml. Add 5 ml of 0·5 per cent. w/v silver nitrate solution, dilute to the mark and set aside in a dark cupboard for exactly 15 minutes. Measure the optical densities, using a Spekker absorptiometer with a tungsten lamp, 4-cm cells and Ilford No. 602 filters. Prepare a calibration graph.

PROCEDURE FOR SOLUTION OF SAMPLES—

Titanium sponge—Weigh 10 g (with the proportionate amounts of coarse and fine material if the sample has been compacted and drilled) and transfer to a 1-litre round-bottomed flask. Add 750 ml of diluted sulphuric acid (1 + 4), connect to a reflux condenser, and heat gently at first until the vigorous reaction ceases. Finally, heat to boiling and continue until solution is complete. Cool slightly, remove the reflux condenser, add 10 ml of nitric acid, sp.gr. 1·42, and boil for 2 minutes to remove nitrous fumes. Cool, filter through a close texture filter-paper into a 1-litre calibrated flask and make up to the mark.

Titanium granules, ingots or wrought products—

(*a*) *Solution in sulphuric acid*—Weigh 1·0 g of sample and transfer to 500-ml round-bottomed flask. Add 75 ml of dilute sulphuric acid (1 + 4), connect to a reflux condenser and heat to boiling. Continue boiling until solution is complete. Cool, remove the reflux condenser, add cautiously 2 ml of nitric acid, sp.gr. 1·42, and boil for 2 minutes. Cool, filter into a 100-ml calibrated flask and make up to the mark.

(*b*) *Solution in hydrofluoric acid*—Weigh 1·0 g of sample and transfer to a plastic beaker or platinum dish. Add 10 ml of water and 4 ml of 40 per cent. hydrofluoric acid.

When the sample is dissolved, add 1·0 g of boric acid, mix thoroughly and set aside until the boric acid is dissolved. Transfer the solution to a 150-ml beaker containing 2 ml of nitric acid, sp.gr. 1·42, and heat the solution until colourless. Cool, filter into a 100-ml calibrated flask and make up to the mark.

NOTE—A blank on reagents must be determined according to the method of solution selected.

PROCEDURE FOR MEASURING TURBIDITY—

From the sample solution prepared by the appropriate method, transfer a 20-ml aliquot to a 100-ml calibrated flask. Add 10 ml of sulphuric - nitric acid mixture, and dilute with water to approximately 80 ml. Add 5 ml of 0·5 per cent. w/v silver nitrate solution, make up to the mark and shake well. Set aside in a dark place for 15 minutes. Measure the optical density with a Spekker absorptiometer, using a tungsten lamp, 4-cm cell and Ilford No. 602 filters. Similarly, determine the blank on reagents; correct for the blank value and calculate the amount of chlorine present by reference to the calibration curve.

CONCLUSIONS

The figures obtained on synthetic solutions by the proposed turbidimetric method indicate that the recovery of chlorine is satisfactory over the range of 0·0001 to 0·0075 g. Furthermore, provided the prescribed precautions about sampling are observed, the turbidimetric results on a number of titanium samples compare favourably with those obtained gravimetrically and are sufficiently accurate for control purposes.

The analysis of batches of ten samples can be completed in about 3 hours by the turbidimetric method. Compared with alternative methods[1,2,3,4] involving the precipitation of silver chloride and long settling periods of up to 48 hours, the new procedure shows a considerable saving in time.

Tests on dissolution of samples in diluted sulphuric acid (1 + 4), without use of a reflux condenser, established that particular care is essential to prevent loss of chlorine. Although less convenient for batches of samples, solution under reflux is advocated, as less attention is necessary and time of solution is reduced. Samples can be dissolved rapidly in hydrofluoric acid, but generally it is found that any advantage gained is outweighed by the inherent disadvantages.

The proposed method is simple, rapid and direct and therefore is recommended particularly for control purposes.

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A Specific Test for Cobalt

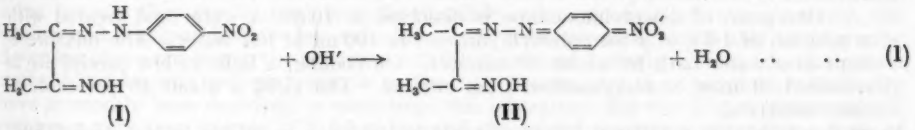
By F. FEIGL and D. GOLDSTEIN*

Translated by R. E. OESPER†

The use of the *p*-nitrophenylhydrazone of diacetylmonoxime as a specific reagent for cobalt is proposed, a violet-coloured complex being formed. Interference from copper and nickel is avoided by the addition of potassium cyanide. The limit of identification is 0·1 μg of cobalt and the dilution limit is 1 in 500,000.

An especially interesting chapter of the chemistry of specific, selective and sensitive reactions[1] deals with the ascription of the analytical effects of organic compounds to certain groups and atoms that are capable of forming salts and entering into co-ordination systems. The factual material to be found here is of use in understanding the multifarious applications of organic reagents[2] and also when studies are being planned to improve existing reagents or to discover new ones. Numerous examples can be cited of the improvement of organic reagents, which succeeded because of the introduction into the molecule of groups that *per se* were not chemically active but that advantageously altered the colour and solubility of the particular reaction products. New organic reagents have been discovered by noting that valuable indications of analytical usefulness are often furnished by studying the structural aspects of a compound from the standpoint of group action and possible tautomeric transformations.

An excellent example is the *p*-nitrophenylhydrazone of diacetylmonoxime (**I**). This compound is a monobasic acid by virtue of the oxime group, in which the hydrogen atom stands in a co-ordinatable position to the nitrogen atom. As an enolisable nitro compound, **I** is soluble in alkali hydroxide, a consequence of the transformation into the alkali salt of the corresponding *aci*-nitro compound. The quinoidal anion (**II**) has a deep violet colour.

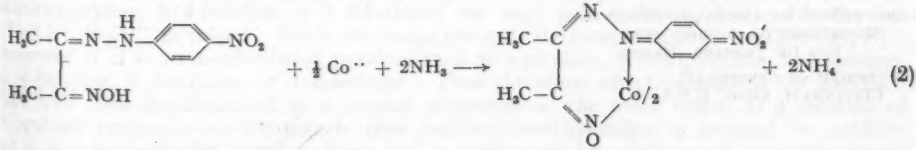


(**I**) (**II**) (1)

Accordingly, the possibility of the *p*-nitrophenylhydrazone of diacetylmonoxime functioning as a dibasic acid is not excluded. The rearrangement shown in (1) occurs to not more than a slight extent with dilute ammonium hydroxide, which provides too low a concentration of hydroxyl ions. Consequently, when ammonium hydroxide is added to a water - ethanol solution of **I** no violet colour appears but only an orange shade, and furthermore after dilution with water the hydrazone can be extracted with ether. This is in conformity with the fact that the violet solution of the hydrazone in sodium hydroxide turns yellow on the addition of a sufficient quantity of solid ammonium salts, and if the liquid is then extracted with ether the solution becomes almost colourless.

Investigation of the analytical behaviour of the *p*-nitrophenylhydrazone of diacetylmonoxime showed that on the addition of an ethanol solution of this compound to ammoniacal solutions of ammine-forming metal ions (palladium, silver, copper, nickel, cobalt) only cobalt ions react in a characteristic fashion. A violet colour (almost identical with that of an alkaline solution of **I**) is obtained, the intensity depending on the cobalt content of the system. Therefore, the reaction of the *p*-nitrophenylhydrazone with cobalt ions is specific.

The coloured product of this reaction has not yet been isolated. The violet inner-complex anion containing cobalt, shown below in reaction (2), is probably formed—



(2)

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According to this representation, the chelate binding of the cobalt is accompanied by the rearrangement of the *p*-nitrophenylhydrazone into its *aci* form, a transformation that is not significantly realisable with ammonium hydroxide. The participation of ammonia is not decisive here, because the colour reaction can be accomplished likewise by other basic compounds (ethylenediamine, calcium oxide, magnesium oxide), which of themselves are not capable of bringing about the enolisation of the nitro compound as shown in reaction (1).

It is most remarkable that the coloured cobalt compound, once it has been formed, is stable to alkali cyanide and ammonium salts, even though it is not formed when the ethanolic reagent solution is added to cobalt solutions containing alkali cyanide or ammonium salts. Similarly, cobalt carbonate is not changed when moistened with the reagent solution, whereas the violet cobalt compound is resistant to alkali carbonate. Accordingly, examples of false equilibria are presented here.

The formation of the violet cobalt compound of the *p*-nitrophenylhydrazone of diacetylmonoxime and its resistance to alkali cyanides make possible a new and rather sensitive test for cobalt, which probably could also serve as the basis of a colorimetric procedure for the determination of this metal. Although many tests for cobalt are known, the one described in this paper may have considerable interest and not only because of its exceedingly characteristic chemistry.

Method

A micro test-tube is used. One drop of the test solution is treated with 1 drop of concentrated ammonium hydroxide and 2 drops of the ethanolic reagent solution. Depending on the quantity of cobalt, a violet or pink colour appears. When slight amounts of cobalt are involved, it is as well to extract the excess of reagent with ether.

The limit of identification is 0·1 μg of cobalt and the dilution limit is 1 in 500,000.

A 0·1 per cent. solution of *p*-nitrophenylhydrazone of diacetylmonoxime in ethanol is used.

The reagent can be prepared as follows—

One gram of diacetylmonoxime is dissolved in 10 ml of water and treated with a solution of 1·5 g of *p*-nitrophenylhydrazine in 100 ml of hot water. The mixture is kept in a water bath for about 30 minutes. On cooling, a light yellow precipitate is obtained; it may be recrystallised from ethanol. The yield is about 40 per cent. of the theoretical.

The procedure is especially recommended for testing ammoniacal solutions, if need be after filtration to remove any considerable amounts of insoluble metal hydroxides. If much copper or nickel is present, the blue colour makes it difficult or impossible to discern slight amounts of cobalt. In such cases, the reagent should be added and followed by dropwise addition of 1 per cent. potassium cyanide solution. The blue $[Cu(NH_3)_4]^{"}$ and $[Ni(NH_3)_4]^{"}$ ions are thus converted to colourless $[Cu_2(CN)_4]^{"}$ and light yellow $[Ni(CN)_4]^{"}$ ions, and even slight amounts of the pink colour due to cobalt are then easily visible. Large amounts of ammonium salts should be removed before the actual test by evaporating the solution to dryness and igniting the residue. Evaporation with dilute nitric acid will then yield a test solution free from ammonium salt.

We are grateful to the Conselho Nacional de Pesquisas for its support of this study.

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The Use of Inorganic Complexes in Colour Reactions for Organic Compounds

Part II. The Determination of the Total Concentration of Non-α-substituted Alkylpyridines in the Presence of α-Substituted Alkylpyridines

By D. P. BIDDISCOMBE and E. F. G. HERINGTON

The quantitative determination of non-α-substituted alkylpyridines in the presence of α-substituted alkylpyridines by the use of a reagent containing trisodium pentacyanoamminoferrate and *p*-nitrosodimethylaniline is described. The method is illustrated by the determination of β-picoline plus γ-picoline in admixture with 2:6-lutidine and 2-ethylpyridine.

Baudisch[1] observed the formation of a violet colour on the interaction of nitrosobenzene and trisodium pentacyanoamminoferrate and reported that pyridine inhibited the formation of this colour while α-picoline did not. He suggested that this difference in behaviour between the two bases was a steric effect, and that it might be utilised for the determination of pyridine in α-picoline. However, no further work on this proposed analytical method appears to have been done, probably because nitrosobenzene is an unstable substance unsuitable for quantitative work and because the determination of pyridine in α-picoline is not a problem of much practical significance. The work now described shows that *p*-nitrosodimethylaniline can satisfactorily be employed in place of nitrosobenzene for the determination of certain homologues of pyridine.

The "β-picoline fraction" of commerce generally contains 2:6-lutidine and 2-ethylpyridine as well as both β-picoline and γ-picoline. Whilst these picolines are of considerable value, because they can be used to make nicotinic and *iso*nicotinic acids, respectively, the lutidine and ethylpyridine are less valuable. It is therefore useful to be able to determine β-picoline plus γ-picoline in the presence of 2:6-lutidine and 2-ethylpyridine. A colorimetric method[2] and an infra-red spectroscopic method[3] for determining these picolines individually have previously been described in work from this laboratory, but the first of these methods requires a very pure sample of 2:6-lutidine and the second requires a water-free sample of the unknown mixture. By the present technique the total concentration of these two picolines is determined in one experiment, pure 2:6-lutidine is not required and aqueous solutions of the bases can be analysed directly. Moreover, by this new method very low concentrations (down to 0·03 per cent.) of β-picoline plus γ-picoline can be determined.

The method is based on a physico-chemical study of the equilibria involved in the system trisodium pentacyanoaquoferrate, *p*-nitrosodimethylaniline and a pyridine base, *B*. The simultaneous equilibria concerned are represented by the following equations—

$$[Fe(CN)_5\cdot H_2O]''' + NO\cdot C_6H_4\cdot N(CH_3)_2 \rightleftharpoons [Fe(CN)_5\cdot NO\cdot C_6H_4\cdot N(CH_3)_2]''' + H_2O \quad (1)$$

$$[Fe(CN)_5\cdot H_2O]''' + B \rightleftharpoons [Fe(CN)_5\cdot B]''' + H_2O \quad .. \quad .. \quad .. \quad (2)$$

In practice it was found convenient to employ trisodium pentacyanoamminoferrate as reagent, rather than trisodium pentacyanoaquoferrate, which is shown in equations (1) and (2), because the former is more easily made in a pure state. However, very dilute solutions were used, so that in fact the ion $[Fe(CN)_5\cdot H_2O]'''$ rather than the ion $[Fe(CN)_5\cdot NH_3]'''$ was involved in the equilibria (1) and (2).

The ion $[Fe(CN)_5\cdot NO\cdot C_6H_4\cdot N(CH_3)_2]'''$ exhibits a strong green colour, whereas it has been shown that the ions $[Fe(CN)_5\cdot B]'''$, where *B* is pyridine, β-picoline, γ-picoline, 4-ethylpyridine, 3:4-lutidine or 3:5-lutidine, are very pale yellow and resemble the ion $[Fe(CN)_5\cdot H_2O]'''$ in colour. Steric hindrance prevents the formation of an ion $[Fe(CN)_5\cdot B]'''$ however, if *B* is an α-substituted pyridine such as α-picoline, 2-ethylpyridine, 2:3-lutidine, 2:4-lutidine, 2:5-lutidine or 2:6-lutidine. Thus the steric effect postulated by Baudisch has now been demonstrated as a general phenomenon: the green colour of a solution of trisodium pentacyanoamminoferrate plus *p*-nitrosodimethylaniline is reduced by addition of a non-α-substituted pyridine base, but is unchanged by addition of an α-substituted pyridine base.

The method described in this paper is generally applicable to the determination of any non-α-substituted alkylpyridine in the presence of α-substituted alkylpyridines. Thus, for example, 3-ethylpyridine can be determined in collidine fractions, in which it frequently occurs in admixture with 2:3:6- and 2:4:6-trimethylpyridine.

REACTION MEDIA—

The equilibria were studied for both aqueous and 40 per cent. v/v aqueous ethanolic mixtures. The chief advantage of using 40 per cent. aqueous ethanolic mixtures is that bases only partly miscible with water can thus be studied, in addition to water-soluble bases, such as β-picoline, γ-picoline, 2:6-lutidine and 2-ethylpyridine. Further, standard solutions of *p*-nitrosodimethylaniline may be made up very easily in ethanol, whereas the required amount of this material is soluble only with difficulty in water. Moreover, whilst ethanolic solutions of this reagent are stable, aqueous solutions are subject to deterioration.

The equilibrium constants for reaction (2) for different non-α-substituted bases show greater variation in 40 per cent. aqueous ethanolic media than in aqueous media (see Table II, p. 716). This constitutes a disadvantage of using ethanol when mixtures containing more than one non-α-substituted base are to be analysed, but the difficulty can be overcome in the determination of β-picoline plus γ-picoline. A further disadvantage of the use of ethanol is that it increases the time required to reach equilibrium. In general, however, it is preferable to employ 40 per cent. aqueous ethanolic media.

In order to minimise any disturbing effects of variation of pH, all mixtures were buffered by addition of sodium borate. It was necessary to halve the concentration of sodium borate in experiments involving use of ethanolic mixtures as compared with those with aqueous mixtures, in order to avoid precipitation of this salt. In some circumstances there was still a slight tendency for a slow deposition of crystals in the ethanolic solutions, but this led to no difficulty or errors. Rough tests with pH indicator papers showed that these ethanolic solutions were adequately buffered.

EXAMINATION OF EQUILIBRIUM (1)—

Equilibrium (1) was studied by the method of continuous variation,[4,5] optical density being used as a measure of the equilibrium concentrations of the ion $[Fe(CN)_5{\cdot}NO{\cdot}C_6H_4{\cdot}N(CH_3)_2]^{''}$ in a series of solutions in which the sum of the initial molar concentrations of the two reactants

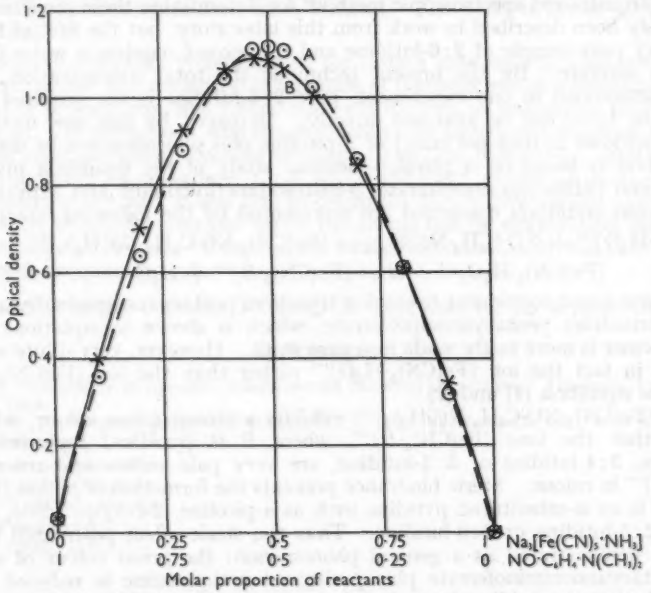

Fig. 1. Results of continuous-variation experiments: curve A, aqueous solutions; curve B, 40 per cent. v/v aqueous ethanolic solutions

was constant. The curve obtained for aqueous solutions (Fig. 1, curve A) shows that a 1 to 1 complex is formed, as required by equation (1). When 40 per cent. v/v aqueous ethanolic solutions are used, the maximum optical density occurs in a mixture in which the initial molar concentrations of the two reactants are not exactly equal (Fig. 1, curve B). This effect may be due to inequality of the activity coefficients of the reactants in this solvent: however, a 1 to 1 complex is clearly involved in these solutions also. The rounded shape of the curves indicates that the reaction does not proceed entirely to the right (equation (1)), for, if it did, the graphs would consist of pairs of intersecting straight lines. Calculation shows that under the conditions of these experiments, in the solutions prepared from equimolar amounts of the two reactants, approximately half of the trisodium pentacyanoamminoferrate is converted into the salt $Na_3[Fe(CN)_5{\cdot}NO{\cdot}C_6H_4{\cdot}N(CH_3)_2]$ at equilibrium.

MATHEMATICAL BASIS OF METHOD—

Introduction of a pyridine base B into the system leads to the additional equilibrium shown in equation (2). Let the equilibrium constants for reactions (1) and (2) be K_1 and K_2, respectively, the activity of the water being included in these constants in the usual way. Let the initial molar concentrations of $NO{\cdot}C_6H_4{\cdot}N(CH_3)_2$, of the base B and of $[Fe(CN)_5{\cdot}H_2O]'''$ be a, b and c, respectively, and let the fractions of $[Fe(CN)_5{\cdot}H_2O]'''$ converted into $[Fe(CN)_5{\cdot}NO{\cdot}C_6H_4{\cdot}N(CH_3)_2]'''$ and into $[Fe(CN)_5{\cdot}B]'''$ at equilibrium be α_1 and α_2, respectively. Then—

$$K_1 = \alpha_1/[(1 - \alpha_1 - \alpha_2)\,(a - \alpha_1 c)] \quad .. \quad .. \quad .. \quad .. \quad (3)$$

$$\text{and } K_2 = \alpha_2/[(1 - \alpha_1 - \alpha_2)\,(b - \alpha_2 c)] \quad .. \quad .. \quad .. \quad .. \quad (4)$$

If conditions are chosen such that both the p-nitrosodimethylaniline and the pyridine base are at much higher concentrations than the pentacyanoamminoferrate, we have $a \gg \alpha_1 c$ and $b \gg \alpha_2 c$, and equations (3) and (4) reduce, respectively, to—

$$K_1 = \alpha_1/[(1 - \alpha_1 - \alpha_2)a] \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

$$\text{and } K_2 = \alpha_2/[(1 - \alpha_1 - \alpha_2)b] \quad .. \quad .. \quad .. \quad .. \quad .. \quad (6)$$

Consider two solutions, the first containing the complex $[Fe(CN)_5{\cdot}NO{\cdot}C_6H_4{\cdot}N(CH_3)_2]'''$ at the concentration $\alpha_1 c$, and a large excess of p-nitrosodimethylaniline, and the second containing p-nitrosodimethylaniline at the same concentration as in the first solution, but containing no complex. The concentration of the complex in the first solution is by Beer's law proportional to the optical-density difference, d, between these two solutions, *i.e.*—

$$\alpha_1 c = kd \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

where k is a constant. From equations (5), (6) and (7) it follows that in a series of experiments in which a and c are kept constant, and $a \gg c$ and $b \gg c$, b is given by the expression—

$$b = k'\,(1/d - 1/d_0) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

where $k' = acK_1/kK_2$, and d_0 is the optical-density difference as defined above when $b = 0$. In practice, a/c was 20 and b/c varied from about 350 to 2·5. Measurements of the optical densities of test solutions containing various known amounts of pyridine (see Table I) confirmed the applicability of equation (8).

In order to apply equation (8) to the determination of a single non-α-substituted pyridine base in a mixture with α-substituted bases, the optical-density differences d_0, d_S and d are measured for solutions containing reagents alone, reagents plus a standard weight, S, of the non-α-substituted base and reagents plus a weight, U, of the unknown base mixture. The weight percentage, p, of the non-α-substituted base in the mixture is given by the following equation, which is derived from equation (8)—

$$p = 100Sd_S\,(d_0 - d)/[Ud\,(d_0 - d_S)] \quad .. \quad .. \quad .. \quad (9)$$

SOURCES OF ERROR—

Consideration of the experimental technique suggested that the main source of random error in determinations would arise from errors in optical-density measurements. Differentiation of equation (9) shows that, for any value of d, the fractional error in p due to error in d_S is at a minimum when (*i*) d_0 is as large as can be conveniently measured by the instrument, and (*ii*) $d_S = \frac{1}{2}d_0$. Similarly, the fractional error in p due to error in d is at a minimum when $d = \frac{1}{2}d_0$ (*i.e.*, when $d = d_S$). In the method finally adopted, the quantities a, c and S satisfy conditions (*i*) and (*ii*), and U is chosen according to the range in which p lies, so that

the maximum fractional error in p arising from an error of 0·01 in d is 0·05 when p is between 0·1 and 100 per cent., and 0·12 when p is between 0·03 and 0·1 per cent.

A further source of error may occur in the analysis of mixtures containing two or more non-α-substituted bases. Equation (9) is not strictly applicable to such mixtures if the bases being determined exhibit unequal K_2 values. The ratio of K_2 for a base (K_{2B}) to that for pyridine (K_{2P}) may be obtained by using the following equation, which is derived from equation (8)—

$$K_{2B}/K_{2P} = d_P (d_0 - d_B)/[d_B(d_0 - d_P)] \quad .. \quad .. \quad .. \quad .. \quad (10)$$

Here d_P and d_B are the optical-density differences for two mixtures in which equimolar concentrations of pyridine and of the base, respectively, are used, the concentrations of the other components being the same in each mixture. Values of K_{2B}/K_{2P} thus measured are shown in Table II. The ratio of these values for β-picoline and γ-picoline in 40 per cent. aqueous ethanolic solutions is 1·09. However, theory suggests the use of a calibration standard containing an equal weight (½S) of each of these two bases. The difference in their K_{2B}/K_{2P} values then leads to no error in p in the analysis of mixtures containing equal amounts of β-picoline and γ-picoline. The greatest errors in p will arise when the ratio of β-picoline to γ-picoline in the unknown mixture is very small or very large. These conclusions were confirmed by experiment.

Experimental

Reagents—

Trisodium pentacyanoamminoferrate was prepared and stored as described by Herington.[6] For use in the determination of time to reach equilibrium and in the continuous-variation experiments, it was essential to prepare standard solutions of this salt from the solid immediately before use, because the solutions deteriorated on keeping. An $M/3500$ solution decomposed at the rate of approximately 1 per cent. in 5 minutes. A more concentrated ($M/3·5$) solution, kept in darkness, deteriorated less rapidly, although an orange-brown precipitate slowly formed. For experiments other than the above-mentioned, solutions freshly prepared by 1000-fold dilution of an $M/3·5$ stock solution, which could be used for at least 3 weeks, were found to be as satisfactory as $M/3500$ solutions freshly made from the solid. In the preparation of each set of test mixtures, all components except the trisodium salt were mixed first. The trisodium salt solution was then prepared and its addition to all the test solutions was completed, in order, as quickly as possible consistent with thorough mixing. Values of d_S and of d_0 were measured for appropriate mixtures placed at the beginning and at the end of each set. By using in equation (9) values of d_S and of d_0 calculated by interpolation between these measured values, according to the times of addition of the trisodium salt solution, allowance was made for the deterioration of this reagent.

p-Nitrosodimethylaniline was prepared by the method described by Cohen.[7] Of a total yield of 21 g (84 per cent. of theoretical), 11 g having a m.p. of 85° to 86° C (uncorr.) were used in the present work. Aqueous solutions of this reagent were found to be unstable, and were therefore freshly prepared for each day's work. Prolonged shaking was required to effect solution, and a mechanical shaker was employed. Solutions of this material in ethanol were easily prepared, and showed no evidence of deterioration over a period of 4 weeks.

Standard solutions of pyridine bases in water and in absolute ethanol were prepared from purified samples of these bases, which were all at least 99·7 moles per cent. pure. The main impurity was water, but the sample of 2-ethylpyridine was found to contain 0·15 per cent. of non-α-substituted base.

All burette taps were lubricated with Apiezon grease, grade L. The use of Vaseline in preliminary experiments occasionally caused turbidity in the mixtures.

Optical-density measurements—

A Spekker photo-electric absorptiometer was used to measure optical densities. The trisodium pentacyano-p-nitrosodimethylanilineferrate complex being green, and the p-nitrosodimethylaniline solutions (both in water and in 40 per cent. aqueous ethanol) being yellow, it was found that red filters (Ilford No. 608) gave suitable sensitivity, and these were used in conjunction with a tungsten lamp, the solutions being placed in a 1-cm glass cell. Most measurements were made in duplicate.

EQUILIBRATION TIME—

The times required to reach equilibrium in the continuous-variation experiments, as shown by full colour development, were determined by using equimolar amounts of the two reagents in buffered solution, both in aqueous and in 40 per cent. v/v aqueous ethanolic media. The procedures were as follows—

Aqueous solutions—5 ml of *M*/20 sodium borate solution and 2·5 ml each of *M*/2500 aqueous solutions of *p*-nitrosodimethylaniline and of trisodium pentacyanoamminoferrate were placed, in the order stated, in a clean dry boiling-tube, mixed thoroughly and transferred immediately to a 1-cm cell for measurement of optical density at noted times. The absorptiometer had previously been adjusted to give a drum reading of 1·5 with water in a 1-cm cell in the light path. Full colour developed in 7 minutes with these solutions.

Aqueous ethanolic solutions (40 *per cent.*)—2·5 ml of *M*/20 sodium borate solution, 2 ml of water, 2·5 ml of absolute ethanol, 1·5 ml of *M*/1250 ethanolic *p*-nitrosodimethylaniline solution and 1·5 ml of *M*/1250 aqueous trisodium pentacyanoamminoferrate solution were similarly mixed, and the corresponding measurements were made. The cell was covered by a small plate of glass to reduce evaporation. Full colour developed in 70 minutes with these solutions.

In experiments in which pyridine bases were determined, the equilibration times were found to be shorter than in the above-described experiments. This was to be expected from theoretical considerations, since in these analytical experiments the concentration of *p*-nitrosodimethylaniline used was greater than in the continuous-variation experiments. However, in all the experiments described below, to ensure the attainment of equilibrium, at least 10 minutes and 90 minutes, respectively, were allowed to elapse between the preparation and optical-density measurement of aqueous and 40 per cent. aqueous ethanolic mixtures.

CONTINUOUS-VARIATION EXPERIMENTS—

Aqueous solutions—Mixtures containing 5 ml of *M*/20 sodium borate solution and various amounts, totalling 5 ml, of *M*/2500 aqueous solutions of *p*-nitrosodimethylaniline and of trisodium pentacyanoamminoferrate were made, and their optical densities were measured as described. Results are shown in Fig. 1, curve A.

Aqueous ethanolic solutions (40 *per cent.*)—Fig. 1, curve B, shows the results of an experiment, similar to the above, in which mixtures were prepared containing 2·5 ml of *M*/20 sodium borate solution, a total of 4 ml of absolute ethanol and *M*/1250 ethanolic *p*-nitrosodimethylaniline solution, and a total of 3·5 ml of water and *M*/1250 trisodium pentacyanoamminoferrate solution. The combined volume of the solutions of the nitroso compound and of the trisodium salt was in each case 3 ml. The tubes containing the mixtures were corked to prevent evaporation before measurement of optical densities as described. As already stated, the maximum of the curve obtained is slightly displaced from the position corresponding to equimolar concentrations of the two reactants. Repetitions of the experiment showed that this shift, although small, is real.

TEST OF EQUATION (8)—

The applicability of equation (8) was tested by using varying concentrations of pyridine. For this purpose equation (8) was conveniently written in the form—

$$q = Sd_S\,(d_0 - d)/[d(d_0 - d_S)] \quad .. \quad .. \quad .. \quad .. \quad (11)$$

Test solutions, both in aqueous and in 40 per cent. v/v aqueous ethanolic media, were prepared containing reagents alone (optical-density difference d_0), reagents and sodium borate at the same concentrations plus a standard amount, S, of pyridine (optical-density difference d_S), and reagents and sodium borate plus smaller known amounts of pyridine (optical-density differences d). The calculated pyridine contents q of the last-mentioned solutions were determined by using equation (11). Drum readings on the Spekker photo-electric absorptiometer for these and all subsequent test solutions were measured after setting the drum at 1·5 for a solution containing *p*-nitrosodimethylaniline and sodium borate only, at the same concentrations as in the test solutions. Subtraction of these drum readings from 1·5 gave the optical-density differences d_0, d_S and d.

Aqueous ethanolic solutions (40 *per cent.*)—Mixtures were prepared containing 2·5 ml of *M*/20 sodium borate solution, absolute ethanol and *M*/20 ethanolic pyridine solution

totalling 1 ml, 3 ml of $M/150$ ethanolic *p*-nitrosodimethylaniline solution and 3·5 ml of $M/3500$ trisodium pentacyanoamminoferrate solution. Table I shows the amounts of pyridine taken, values of d, d_S and d_0 and the calculated pyridine contents, q. The mixtures containing 3·96 mg of pyridine were used as calibration standards (*i.e.*, $S = 3{\cdot}96$). The calculated values are in good agreement with the amounts taken, thus confirming the applicability of equation (8). Experiments with aqueous solutions gave similar results.

TABLE I

TEST OF THE EQUATION $q = Sd_S(d_0 - d)/[d(d_0 - d_S)]$: PYRIDINE IN 40 PER CENT. v/v AQUEOUS ETHANOLIC MIXTURES

Pyridine taken, mg	Optical density difference (d)	Pyridine found (q), mg
3·96	0·45(d_S)	—
0·00	1·255(d_0)	—
2·77	0·555	2·79
1·98	0·66	1·99
1·38	0·78	1·34
0·99	0·865	0·99
0·47	1·035	0·46
0·24	1·135	0·22
3·96	0·45(d_S)	—
0·00	1·245(d_0)	—

DETERMINATION OF K_{2B}/K_{2P} VALUES—

Values of K_{2B}/K_{2P} were determined by using equation (10).

Aqueous solutions—The value of d_P was measured for a mixture containing 5 ml of $M/20$ sodium borate solution, 1 ml of aqueous $M/50$ pyridine solution, 3·2 ml of aqueous $M/200$ *p*-nitrosodimethylaniline solution and 0·8 ml of $M/1000$ trisodium pentacyanoamminoferrate solution. The value of d_B for each base was found similarly, 1 ml of an $M/50$ aqueous solution of the base being used in place of the pyridine solution in the above mixture. Results are shown in Table II, column 2.

TABLE II

VALUES OF K_{2B}/K_{2P}

Base	K_{2B}/K_{2P} for aqueous mixtures	K_{2B}/K_{2P} for 40 per cent. v/v aqueous ethanolic mixtures
Pyridine	1·00	1·00
α-Picoline	0	0
β-Picoline	0·98	0·83
γ-Picoline	1·01	0·91
2-Ethylpyridine	0	0
4-Ethylpyridine	1·04	0·94
2:3-Lutidine	0	0
2:4-Lutidine	0	0
2:5-Lutidine	0	0
2:6-Lutidine	0	0
3:4-Lutidine	1·06	0·79
3:5-Lutidine	0·94	0·63

Aqueous ethanolic solutions (40 *per cent.*)—The value of d_P was measured for a mixture containing 2·5 ml of $M/20$ sodium borate solution, 1 ml of $M/30$ ethanolic pyridine solution, 3 ml of $M/150$ ethanolic *p*-nitrosodimethylaniline solution and 3·5 ml of $M/3500$ trisodium pentacyanoamminoferrate solution. The value of d_B for each base was found similarly, 1 ml of an $M/30$ ethanolic solution of the base being used in place of the pyridine solution in the above mixture. Results are shown in Table II, column 3.

METHOD FOR THE DETERMINATION OF β-PICOLINE PLUS γ-PICOLINE IN THE PRESENCE OF 2-ETHYLPYRIDINE AND 2:6-LUTIDINE

REAGENTS—

Sodium borate solution—Dissolve 4·768 g of sodium borate decahydrate in distilled water and make up to 250 ml.

Trisodium pentacyanoamminoferrate solution—Dissolve 1·086 g of trisodium pentacyanoamminoferrate in distilled water, make up to 10 ml, and keep in darkness. Prepare a working solution immediately before use by diluting 0·05 ml to 50 ml with distilled water.

p-*Nitrosodimethylaniline solution*—Dissolve 0·250 g of *p*-nitrosodimethylaniline in absolute ethanol and make up to 250 ml.

PROCEDURE—

Prepare a standard β-picoline plus γ-picoline solution by dissolving 0·0775 of pure β-picoline and 0·0775 g of pure γ-picoline in absolute ethanol and making up to 50 ml.

Prepare a solution in absolute ethanol containing U g (see Table III) of the unknown base sample per ml. Use 1 ml of this solution (see below), but for the range $p = 0·03$ to 0·3 per cent. it is sufficiently accurate to take 1·0 g of the unknown base sample without adding ethanol.

TABLE III

REQUIRED SAMPLE WEIGHTS AND FACTORS FOR USE IN CALCULATIONS IN β-PICOLINE PLUS γ-PICOLINE DETERMINATIONS

β-Picoline plus γ-picoline content of sample (*p*), % w/w	Amount of sample required (U), g	Factor (F) for use in equation (12)
30 to 100	0·0031	100
3 to 30	0·031	10
0·3 to 3	0·31	1
0·03 to 0·3	1·0	0·31

Place 2·5 ml of sodium borate solution and 3·0 ml of *p*-nitrosodimethylaniline solution in each of four clean dry boiling-tubes, numbered from 1 to 4. Add 1·0 ml of the standard β-picoline plus γ-picoline solution to tube 1, and 1·0 ml of the unknown base sample solution to tube 2. Add 1·0 ml of absolute ethanol to each of tubes 3 and 4. Shake the tubes and then add 3·5 ml of trisodium pentacyanoamminoferrate solution to each of tubes 1, 2 and 3, and 3·5 ml of distilled water to tube 4. Shake the tubes, and set them aside, corked, for at least 90 minutes before measurement of optical densities.

Adjust the Spekker absorptiometer to give a drum reading of 1·5, using Ilford No. 608 filters, with a 1-cm cell filled with the solution from tube 4 in the light path. Record the drum readings with the 1-cm cell filled with the solutions from tubes 1, 2 and 3. Let these readings be r_1, r_2 and r_3, respectively. Then $d_S = 1·5 - r_1$, $d = 1·5 - r_2$ and $d_0 = 1·5 - r_3$. Calculate the weight percentage, *p*, of β-picoline plus γ-picoline in the sample from the equation—

$$p = Fd_S(d_0 - d)/[d(d_0 - d_S)] \quad .. \quad .. \quad .. \quad .. \quad (12)$$

using the value of F appropriate to the value of U employed, as indicated in Table III.

TABLE IV

DETERMINATION OF β-PICOLINE PLUS γ-PICOLINE IN MIXTURES WITH 2:6-LUTIDINE AND 2-ETHYLPYRIDINE

Total weight of sample taken (U), g	Synthetic mixtures containing: β-picoline, % w/w	γ-picoline, % w/w	2:6-lutidine, % w/w	2-ethylpyridine, % w/w	β-Picoline plus γ-picoline: taken, % w/w	found (*p*), % w/w
0·0031	10	70	10	10	80	83·4
	25	25	25	25	50	47·7
	25	25	50	0	50	48·3
	10·1	20	35	34·9	30·1	29·7
0·031	15·1	15·0	35·0	34·9	30·1	31·0
	0·04	10·04	45·0	44·9	10·08	10·66
	3·04	0·04	48·5	48·4	3·08	2·79
0·31	0·04	1·04	49·5	49·4	1·08	1·15
	0·191	0·190	49·8	49·8	0·381	0·367
1·0	0·071	0·040	50·0	49·9	0·111	0·118
	0·041	0·070	50·0	49·9	0·111	0·123
	0·056	0·055	50·0	49·9	0·111	0·122
	0·047	0·046	50·0	49·9	0·093	0·099
	0·016	0·015	100·0	0·0	0·031	0·030

Results

The results of thirty determinations showed that the standard deviation of a single determination was 6 per cent. of the total non-α-substituted alkylpyridine base present when the synthetic mixtures contained between 0·3 and 100 per cent. of β-picoline plus γ-picoline. Some typical values are shown in Table IV, which also presents the results of the analyses of mixtures containing between 0·03 and 0·1 per cent. of β-picoline plus γ-picoline.

Analyses by this method of the 2:6-lutidine and 2-ethylpyridine samples used in preparing the synthetic mixtures showed non-α-substituted base contents equivalent, respectively, to 0·013 and 0·149 per cent. w/w of β-picoline plus γ-picoline. The additional non-α-substituted base thus introduced into the synthetic mixtures is included in the amounts of β-picoline and γ-picoline shown in columns 2, 3 and 6 of Table IV.

The work described above has been carried out as part of the research programme of the Chemical Research Laboratory, and this paper is published by permission of the Director of the Laboratory.

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The Use of Inorganic Complexes in Colour Reactions for Organic Compounds

Part III. The Determination of *iso*Quinoline in the Presence of Quinoline and Quinaldine

By D. P. Biddiscombe and E. F. G. Herington

The quantitative determination of *iso*quinoline in the presence of quinoline and quinaldine by the use of a reagent containing trisodium pentacyanoamminoferrate and *p*-nitrosodimethylaniline is described. The results of analyses of artificial mixtures are presented and the use of the method in following the separation of quinoline and *iso*quinoline by fractional distillation is recorded.

In Part II,[1] a method for the determination of the total concentration of non-α-substituted alkylpyridines in the presence of α-substituted alkylpyridines was described. The procedure was based on the study of the simultaneous equilibria—

$$[Fe(CN)_5{\cdot}H_2O]''' + NO{\cdot}C_6H_4{\cdot}N(CH_3)_2 \rightleftharpoons [Fe(CN)_5{\cdot}NO{\cdot}C_6H_4{\cdot}N(CH_3)_2]''' + H_2O \quad (1)$$

$$[Fe(CN)_5{\cdot}H_2O]''' + B \rightleftharpoons [Fe(CN)_5{\cdot}B]''' + H_2O \quad .. \quad .. \quad .. \quad (2)$$

where B was a pyridine base.

With use of 40 per cent. v/v aqueous ethanolic solutions, and under experimental conditions as described in Part II, the values of K_{2B}/K_{2P} for *iso*quinoline, quinoline and quinaldine were found to be 1·08, 0·00 and 0·00, respectively. These figures show that *iso*quinoline behaves like the non-α-substituted alkylpyridines in forming a complex of the type $[Fe(CN)_5{\cdot}B]'''$, whilst quinoline and quinaldine, like the α-substituted alkylpyridines, do not form complexes of this type. This difference in behaviour, which is attributed to steric hindrance, has been used to develop a method for the determination of *iso*quinoline in the presence of quinoline and quinaldine. These three bases, whose boiling points are 243°, 238° and 247° C, respectively, occur in close association in coal-tar fractions.

The conditions chosen for carrying out the analyses were determined by the theoretical and practical considerations discussed in Part II. The applicability of the equation (see Part II, equation 11)—

$$q = Sd_S (d_0 - d)/[d (d_0 - d_S)]$$

to the determination of the concentration, q, of *iso*quinoline was tested experimentally (see Table I). The percentage, p, of *iso*quinoline in a mixture containing quinoline and quinaldine is calculated from the optical-density measurements by means of the equation—

$$p = Fd_S (d_0 - d)/[d (d_0 - d_S)],$$

where the value of F depends upon the amount of sample taken (see Table II).

Table III shows some results obtained in this way when synthetic *iso*quinoline - quinoline mixtures were analysed.

By suitable choices of the weights of sample taken for analysis (see Table II), it is possible to determine *iso*quinoline contents in the range 0·03 to 100 per cent. w/w. The method is particularly well adapted for the determination of small concentrations of *iso*quinoline in quinoline and quinaldine, and has been used to follow the purification of quinoline by distillation (see Table IV). A search of the literature has failed to reveal any existing method for the determination of concentrations of *iso*quinoline throughout this range.

Experimental

The reactions were carried out in 40 per cent. aqueous ethanolic solutions and were allowed to proceed for 90 minutes before the optical-density readings were taken.

Test of the equation $q = Sd_S (d_0 - d)/[d (d_0 - d_S)]$—

The experimental conditions were similar to those described for 40 per cent. aqueous ethanolic solutions on p. 715, Part II. Table I shows the amounts of *iso*quinoline taken, values of d, d_S and d_0, and the calculated *iso*quinoline contents, q. The mixtures containing 4·30 mg of *iso*quinoline were used as calibration standards (*i.e.*, S = 4·30). The agreement between calculated and observed values indicates that the theory developed in Part II is applicable to the systems containing *iso*quinoline.

Table I

Test of the equation $q = Sd_S (d_0 - d)/[d (d_0 - d_S)]$: *iso*quinoline in 40 per cent. v/v aqueous ethanolic mixtures

*iso*Quinoline taken, mg	Optical density difference (d)	*iso*Quinoline found (q), mg
4·30	0·51(d_S)	—
0·00	1·11(d_0)	—
2·15	0·70	2·14
1·08	0·86	1·06
0·52	0·97	0·52
4·30	0·51(d_S)	—
0·00	1·105(d_0)	—

Method for the determination of *iso*quinoline in the presence of quinoline and quinaldine

Reagents—

Prepare *sodium borate solution*, *trisodium pentacyanoamminoferrate solution* and p-*nitroso-dimethylaniline solution* as specified in Part II (p. 716).

Table II

Required sample weights and factors for use in calculations in *iso*quinoline determinations

*iso*Quinoline content of sample (p), % w/w	Amount of sample required (U), g	Factor (F) for use in equation for calculating p
30 to 100	0·0043	100
3 to 30	0·043	10
0·3 to 3	0·43	1
0·03 to 0·3	1·1	0·39

PROCEDURE—

Prepare a standard *iso*quinoline solution by dissolving 0·2150 g of pure *iso*quinoline in absolute ethanol and making up to 50 ml.

Prepare a solution in absolute ethanol containing U g (see Table II) of the unknown base sample per ml. For the range $p = 0{\cdot}03$ to 0·3 per cent. it is sufficiently accurate to take 1·1 g of the unknown base sample without adding ethanol.

Proceed as directed in Part II, using the appropriate base solutions, to obtain the corresponding values of d_S, d and d_0. When 1·1-g samples of base are used, warm all the test solutions to about 30° C by immersing the tubes in a bath of water at this temperature for about 10 minutes before measurement of optical densities. This procedure is necessary in order to avoid cloudiness of the solutions, caused by their separation into two phases.

Calculate the weight percentage, p, of *iso*quinoline in the sample from the equation—

$$p = Fd_S (d_0 - d)/[d (d_0 - d_S)],$$

using the value of F appropriate to the value of U employed, as indicated in Table II.

RESULTS

Synthetic mixtures of *iso*quinoline and quinoline containing between 0·058 and 90 per cent. of *iso*quinoline were analysed by the method described: the results are shown in Table III. These results show that the standard deviation of a single determination was 3·4 per cent. of the total *iso*quinoline present.

TABLE III

DETERMINATION OF *iso*QUINOLINE IN MIXTURES WITH QUINOLINE

Total weight of sample taken, U	0·0043 g				0·043 g				0·43 g				1·1 g			
*iso*Quinoline taken, % w/w	90·0	70·0	50·0	30·0	30·0	20·0	10·0	3·00	3·00	2·00	1·00	0·300	0·320	0·220	0·118	0·0580
*iso*Quinoline found, % w/w	89·3	68·8	49·3	31·6	30·8	20·8	10·3	2·93	3·15	2·10	1·01	0·299	0·310	0·214	0·122	0·0550

For preparing the mixtures containing less than 0·2 per cent. of *iso*quinoline, a specimen of quinoline containing 0·12 per cent. of *iso*quinoline was treated with a solution of trisodium pentacyanoamminoferrate in order to decrease its *iso*quinoline content. Ten millilitres of the quinoline specimen were mechanically shaken for 3 hours with 10 ml of a freshly prepared 10 per cent. aqueous solution of the trisodium salt. The base layer was separated, and submitted again to the same treatment. The base was then washed with four 10-ml portions of water, dried over anhydrous sodium sulphate and distilled. About 8 ml of quinoline were obtained: its *iso*quinoline content had been reduced from 0·12 to 0·055 per cent.

The analytical method described was also applied to the examination of a series of fractions obtained in the distillation of a sample of quinoline containing *iso*quinoline. Table IV shows the boiling range at a pressure of 20 mm of mercury and the percentage by weight of *iso*quinoline found in each fraction. These values show that *iso*quinoline, whose normal boiling point is 5° C higher than that of quinoline, concentrated in the last fraction, as would be expected.

TABLE IV

ANALYSIS OF QUINOLINE DISTILLATION FRACTIONS

Boiling range of fraction at pressure of 20 mm of mercury, °C	114° to 116°	116° to 117°	117° to 118°	over 118°	over 118°
*iso*Quinoline found, % w/w	0·30	0·28	0·31	0·23	2·40

The work described above has been carried out as part of the research programme of the Chemical Research Laboratory, and this paper is published by permission of the Director of the Laboratory.

REFERENCE

1. Biddiscombe, D. P., and Herington, E. F. G., *Analyst*, 1956, **81**, 711.

NOTE—Reference 1 is to Part II of this series.

CHEMICAL RESEARCH LABORATORY
TEDDINGTON, MIDDX.

September 18th, 1956

Recommended Methods for the Analysis of Trade Effluents

PREPARED BY THE JOINT A.B.C.M. - S.A.C. COMMITTEE ON METHODS FOR THE ANALYSIS OF TRADE EFFLUENTS

Methods for the Determination of Organic Carbon, Chloride (Chlorion), Acidity, Alkalinity and Manganese

Organic Carbon

THERE is no one general method for the determination of organic carbon; the methods used include modifications designed to eliminate errors arising from the presence of one or more types of compound in the sample. A dry-combustion method cannot be used for sewage and sewage effluent, since loss of organic carbon would occur during the preparation of the sample. In the wet oxidation with hot chromic and sulphuric acids, used in the methods described below, volatile organic compounds, oxalates and thiocyanates may all cause errors unless special precautions are taken to ensure complete oxidation.

The method recommended is a modification of that described by Mills[1] for sewage, a combustion tube being introduced to ensure complete oxidation. The method is, therefore, applicable to sewage, sewage effluents and the majority of trade wastes. When interfering substances are known to be absent, the method may be simplified by omission of the combustion tube.

METHOD A: INTERFERING SUBSTANCES (*e.g.*, VOLATILE ORGANIC COMPOUNDS, OXALATES AND THIOCYANATES) NOT KNOWN TO BE ABSENT

REAGENTS—

Sulphuric acid, sp.gr. 1·84—It may be convenient to mix together several batches of acid. The number of blank determinations is thereby reduced.

Chromic acid—A saturated solution of chromium trioxide in distilled water.

Barium hydroxide, approximately 0·1 N*—Dissolve 18 g of barium hydroxide, $Ba(OH)_2.8H_2O$, of analytical-reagent quality, or 20 g of the commercial grade, in 1 litre of distilled water in a flask. Insert the stopper and then shake the flask until all the crystals have dissolved. Allow the solution to stand for 2 days or until all the carbonate has settled. Siphon the clear solution into a storage bottle connected to a 25-ml automatic pipette. Exclude carbon dioxide by attaching soda-lime guard tubes.

Hydrochloric acid, exactly 0·1 N*—Dilute 10 ml of hydrochloric acid, sp.gr. 1·18, to 1 litre with distilled water. Standardise against pure dry sodium carbonate and dilute to exactly 0·1 *N*.

Phenolphthalein indicator solution—Dissolve 0·1 g of phenolphthalein in 50 ml of industrial methylated spirit and dilute to 100 ml with distilled water.

APPARATUS—

The apparatus is shown diagrammatically in Fig. 1. The flask A (Fig. 2), which has a capacity of 250 ml, has a fused-in side-arm reaching almost to the bottom of the bulb and a neck 9 inches long and with an internal diameter of approximately ½ inch. The neck of the flask is connected, preferably by a ground-glass joint, to a combustion tube, B, 16 inches long and with an internal diameter of ½ inch. The tube is wrapped in asbestos paper and surrounded for two-thirds of its length by

* If it is desired to use barium hydroxide solution and hydrochloric acid such that 1 ml ≡ 1 mg of carbon, use 30 g (33 g of the commercial grade) and 15 ml, respectively, for preparing the solutions.

a metal jacket, C. The combustion tube contains a column of copper oxide (wire form), D, nearest the flask, a column of fused lead chromate (14 to 20 mesh), E, and a roll of reduced copper gauze, F, 1½ inches long; the columns are separated by asbestos plugs and are 4 inches and 3 inches long, respectively. Three specially

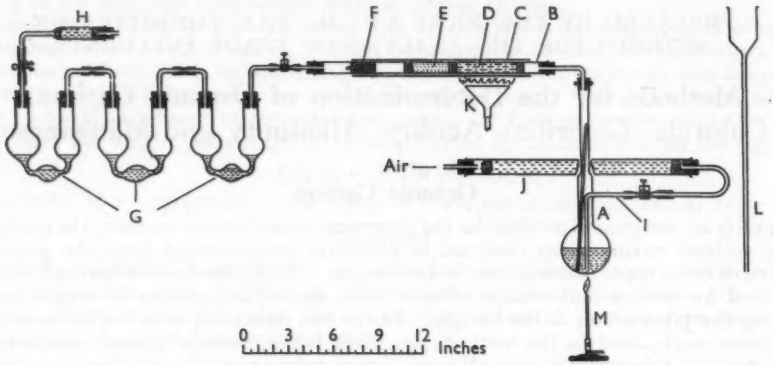


Fig. 1. Apparatus for the determination of organic carbon

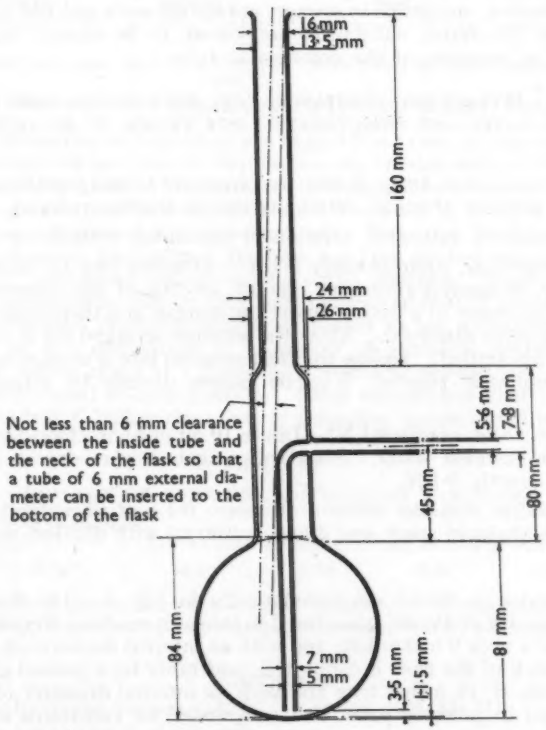


Fig. 2. Details of flask. The total volume of the flask is 320 ml; the material used must be borosilicate glass. Scale: one-third of full size

made absorption tubes,* G (see Fig. 3), and a soda-lime tube, H, are connected in series to the other end of the combustion tube. The side-arm, I, of the flask, A, is connected to a source of air free from carbon dioxide. This may be obtained by passing air through a long tube, J, packed with granules of soda-lime. A burner, K, is arranged beneath the jacketed part of the combustion tube so that the column of copper oxide is the most strongly heated. If the lead chromate is too strongly heated, it will fuse together as one mass.

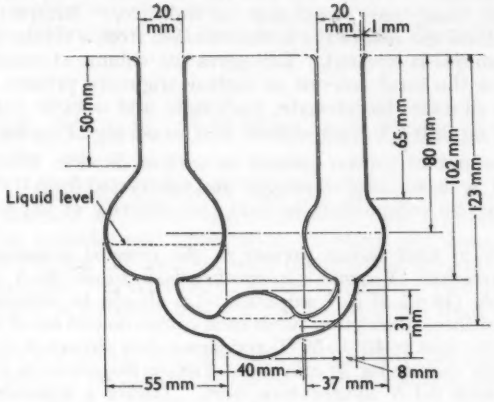


Fig. 3. Details of absorption tube. The total volume of the tube is 172 ml, and the approximate levels of the liquid when the tube is being used and contains 25 ml of absorbent are shown by the dotted lines. Scale: one-third of full size

If large amounts of chloride (up to about 5000 mg of Cl′ per litre) are present in the sample, a bubbler containing distilled water should be inserted between flask A and the combustion tube. If the content of chloride is greater than about 5000 mg of Cl′ per litre, uncontrollable evolution of vapours occurs when the reagents are mixed with the sample and accurate results cannot then be obtained.

Reduction of the copper gauze—The copper gauze must be reduced before each determination. Heat the roll of gauze to redness in a bunsen flame and drop it into a borosilicate-glass test-tube containing about 1 ml of methanol. Insert the stopper in the tube and allow the gauze to cool before removing it.

PROCEDURE—

Total carbon—Into each absorption tube measure 25·0 ml of barium hydroxide solution. Connect the tubes in series and close the ends with clips, but do not yet attach them to the combustion tube. Light the burner under the combustion tube and pass a slow stream of air free from carbon dioxide through the flask and combustion tube for at least 30 minutes. Stop the flow of air, connect the absorption tubes to the combustion tube and open the clips. Transfer into the flask a suitable volume of the effluent sample, not more than 50 ml and containing not more than 20 mg of organic carbon. Add 150 ml of sulphuric acid by means of the long-stemmed funnel, L (Fig. 1), so that it forms a layer beneath the sample. Into the flask measure with a safety pipette 10 ml of saturated chromic acid solution, put in a 0° to 200° C thermometer, and immediately re-connect the flask to the combustion tube. Light the micro-burner, M, beneath the flask and gently shake the flask to mix the contents. As the temperature in the flask is raised, evolution of gas occurs, and during this stage the heating should be adjusted so that the current of gas does not overload the

* Other types of absorption tubes could be used, but existing tubes sold commercially would have the disadvantage that either the contents would have to be washed out for titration or the volume of absorbent and the "dead space" would be greater and thus larger errors might arise.

absorption tubes. Allow the temperature in the flask to rise to 145° to 155° C and then adjust the burner so that the temperature is kept within these limits for 2 hours. At the end of this period the contents of the flask should be deep green in colour. The contents of the flask should never be heated so strongly that white fumes of sulphur trioxide are formed.

Stop heating the flask and pass air free from carbon dioxide through the liquid for 30 minutes, at a rate of about two to three bubbles per second, to sweep out any residual carbon dioxide. Titrate the contents of each absorption tube with 0·1 *N* hydrochloric acid, using phenolphthalein as indicator. Subtract the sum of the titres of the test from the *sum* of the titres obtained from a similar blank experiment from which the sample is omitted. This gives the volume of standard hydrochloric acid equivalent to the total amount of carbon originally present in the sample as dissolved carbon dioxide, bicarbonate, carbonate and organic carbon.

1 ml of 0·1 *N* hydrochloric acid ≡ 0·6 mg of carbon.

The total amount of carbon present as carbon dioxide, bicarbonate and carbonate must next be determined separately and subtracted from the total determined as described above by combustion, so that the quantity of the organic carbon can be found.

Determination of total carbon present in the form of dissolved carbon dioxide, bicarbonate and carbonate—Measure into another flask, similar to A, 200 ml of sample. Acidify the sample (10 ml of 5 *N* sulphuric acid should be sufficient) and connect the flask to a set of three absorption tubes each containing 25 ml of barium hydroxide solution. Warm the flask to 40° to 50° C and pass a slow stream of air free from carbon dioxide through the sample for 30 minutes. Titrate the contents of each absorption tube, as before, with 0·1 *N* hydrochloric acid. Titrate a separate 25-ml quantity of barium hydroxide solution with the acid and, by subtraction, calculate the volume of standard acid equivalent to the carbon dioxide absorbed. Hence calculate the amount of carbon present in the sample as dissolved carbon dioxide, bicarbonate and carbonate.

Method B: Interfering substances (*e.g.*, volatile organic compounds, oxalates, thiocyanates) known to be absent

When volatile organic compounds, oxalates, thiocyanates, or other organic substances likely to evolve carbon dioxide or carbon monoxide on acidification, are absent, dissolved carbon dioxide and carbon present as carbonates can be removed from the acidified sample before the oxidation is begun, and the following simple procedure can be used. It is still necessary to prevent acid fumes and halogens from reaching the absorption tubes, but for this purpose an absorption tube containing a small volume of acidified potassium iodide may replace the combustion tube.

Procedure—

Measure a suitable volume of sample into the flask, A, but not more than 50 ml and containing not more than 20 mg of organic carbon, and then add 150 ml of sulphuric acid. Pass a slow stream of air free from carbon dioxide through the liquid for 30 minutes. Meanwhile, measure 25 ml of barium hydroxide solution into each of the three absorption tubes and connect them in series with the absorption tube containing acidified potassium iodide, which replaces the combustion tube. Close the tubes at one end with a clip and at the other with a soda-lime guard tube.

When preparations are complete, stop the flow of air and add to the contents of the flask 10 ml of saturated chromic acid solution. Immediately connect the flask to the absorption train and open the clips. Light the micro-burner and raise the temperature until a steady stream of bubbles occurs. Do not let the gases overload the absorption train and do not heat the flask so strongly that white fumes of sulphur trioxide are evolved. Complete the determination as in Method A, starting at the paragraph beginning "Stop heating the flask and pass air free from carbon dioxide. . . ."

Reference

1. Mills, E. V., *J. Soc. Chem. Ind.*, 1931, **50**, 375T.

Chloride (Chlorion)

Two methods are recommended, namely, that due to Mohr and that due to Volhard. The latter method is included for use when the effluent contains phosphate, since this interferes in the Mohr method.

Mohr's method

PRINCIPLE OF METHOD—

The chloride, in substantially neutral solution containing chromate, is titrated with silver nitrate. Silver chloride is precipitated and red silver chromate is formed at the end-point.

RANGE—

For chloride ion contents of 0·15 to 10 mg in the volume titrated.

APPLICABILITY—

The method is generally applicable, but ions that form insoluble salts with silver interfere. Bromide and iodide are included as their equivalents of chloride. Sulphides, sulphites, cyanides and thiocyanates interfere, but these can be removed or destroyed by acidifying the solution with dilute nitric acid and then boiling it with hydrogen peroxide. Alternatively, if the cyanide or thiocyanate content is known, its equivalent in terms of chloride can be deducted from the result of the titration.

Phosphate also interferes, and when this is present the chloride should be determined by Volhard's method of titration in acid solution (see below).

REAGENTS—

Aluminium hydroxide suspension—Dissolve 125 g of potash alum in 1 litre of distilled water. Precipitate the aluminium by adding ammonium hydroxide slowly and with stirring. Wash the precipitate by decantation with distilled water until it is free from chloride.

Silver nitrate solution, 0·1 N *or* 0·01 N.*

Potassium chromate indicator solution—Dissolve 5 g of potassium chromate in 100 ml of distilled water. Add silver nitrate solution to produce a slight red precipitate of silver chromate and then filter the indicator solution.

PROCEDURE—

Measure a portion of the effluent sample that is expected to contain between 0·15 and 10 mg of chloride ion. If necessary, dilute this to 100 ml.

NOTE—If the sample is coloured, decolorise the portion by adding 3 ml of aluminium hydroxide suspension. Stir the mixture thoroughly and, after a few minutes, filter it and wash the precipitate with 10 to 15 ml of distilled water, collecting the washings.

If necessary, add dilute sulphuric acid or dilute sodium hydroxide solution so that the liquid just decolorises phenolphthalein. Add 1 ml of potassium chromate indicator solution and titrate with silver nitrate solution (0·1 *N* or 0·01 *N*, depending upon the expected amount of chloride) with constant stirring, until a colour change from pure yellow to pinkish yellow is perceptible. It is easier to see the change of colour at the end-point if it is compared with an incompletely titrated sample in a similar filtration vessel.

Carry out a blank titration on 100 ml of distilled water.

Express the results as mg of chloride ion per litre of sample.

1 ml of 0·1 *N* silver nitrate solution ≡ 3·546 mg of chloride ion (Cl').

* If it is desired to use a silver nitrate solution such that

1 ml ≡ 1 mg of chloride ion,

prepare the solution by dissolving 4·79 g of silver nitrate in distilled water and diluting to 1 litre. Standardise this solution against a sodium chloride solution containing 0·1649 g of dried sodium chloride per litre (*i.e.*, 1 ml ≡ 0·1 mg of chloride).

VOLHARD'S METHOD

PRINCIPLE OF METHOD—

The chloride is titrated in acid solution with an excess of silver nitrate, the precipitated chloride is coagulated by shaking with a little nitrobenzene, and the excess of silver is titrated with thiocyanate solution, with ferric alum as indicator.

RANGE—

For amounts of chloride ion above 10 mg per litre of sample.

APPLICABILITY—

The method is generally applicable, but anions whose silver salts are insoluble in dilute nitric acid interfere. Thiocyanate, cyanide and sulphide are destroyed as described under "Mohr's Method"; bromide and iodide are included as their equivalent of chloride. Phosphates do not interfere. Ferrocyanides and ferricyanides, if present in significant amounts, must be removed, *e.g.*, by precipitation with ferric or ferrous sulphate, respectively, followed by filtration.

REAGENTS—

Nitric acid, sp.gr. 1·42.

Silver nitrate solution, 0·1 N *or* 0·01 N.*

Potassium thiocyanate solution, 0·1 N *or* 0·01 N.*

Ferric alum indicator solution—Dissolve 25 g of ferric alum in 100 ml of distilled water; clear the solution by the addition, drop by drop, of dilute sulphuric acid.

Nitrobenzene, redistilled.

PROCEDURE—

Measure a portion of the effluent sample that is expected to contain between 1 and 70 mg of chloride ion. If necessary, dilute this to 100 ml. Acidify with 5 ml of nitric acid. Titrate the solution with silver nitrate solution (0·1 *N* or 0·01 *N*, depending upon the expected amount of chloride) with stirring to coagulate the precipitate. Add about a 2-ml excess of silver nitrate solution if the 0·1 *N* solution is being used (or a 5-ml excess if the 0·01 *N* solution is used). Add about 1 ml of nitrobenzene and stir well. Add 1 ml of ferric alum indicator solution and titrate the excess of silver with potassium thiocyanate solution of appropriate concentration, stirring the mixture well after each addition. The end-point is the appearance of the orange or reddish ferric thiocyanate colour. From the burette readings and the exact concentrations of the solutions ascertain the net amount of silver nitrate used to precipitate the chloride. Express the result as mg of chloride ion per litre of sample.

1 ml of 0·1 *N* silver nitrate solution ≡ 3·546 mg of chloride ion (Cl').

Acidity

DEFINITION—

Titratable acidity is defined as the number of millilitres of 0·1 *N* alkali that are required to raise the pH of a litre of an acid effluent to 4.

REAGENTS—

Methyl orange indicator solution—A 0·04 per cent. solution in 20 per cent. ethanol.

or

Screened methyl orange indicator solution—Dissolve 1 g of methyl orange and 1·4 g of xylene cyanol FF in 500 ml of ethanol.

* If it is desired to use solutions such that

1 ml of silver nitrate solution ≡ 1 mg of chloride ion,

prepare the solution of silver nitrate by the method given in the footnote to "Mohr's Method." Prepare the potassium thiocyanate solution by dissolving 2·741 g of pure potassium thiocyanate in distilled water and diluting to 1 litre. This solution does not keep well and it should be frequently standardised by titration into a known volume of the silver nitrate solution diluted with distilled water and acidified with dilute nitric acid, with ferric alum as indicator, as in carrying out the test.

or

Bromophenol blue indicator solution—A 0·04 per cent. solution in 20 per cent. ethanol.

Sodium hydroxide solution, 0·1 N.

PROCEDURE—

Colourless (or nearly colourless) effluents—Remove any suspended matter from the sample by filtration or centrifuging, and transfer 100 ml of the clear liquid by pipette into a 750-ml conical flask. Add 5 drops of one of the indicator solutions and dilute the solution with 400 ml of freshly boiled and cooled distilled water.

NOTE—If the colour of the indicator is bleached, repeat the determination, adding a crystal or two of sodium thiosulphate before the addition of the indicator.

Titrate with 0·1 *N* sodium hydroxide solution, and express the result as the number of millilitres of 0·1 *N* alkali per litre of sample.

If the titration exceeds 30 ml of 0·1 *N* alkali, use a smaller quantity of sample.

Deeply coloured effluents—If the colour of the effluent diluted as described above interferes with the determination of the end-point, an electrometric titration must be used.

Alkalinity

DEFINITION—

Titratable alkalinity is defined as the number of millilitres of 0·1 *N* acid required to lower the pH of a litre of an alkaline effluent to 8 ("phenolphthalein alkalinity") or to 4 ("methyl orange alkalinity").

REAGENTS—

Methyl orange indicator solution—A 0·04 per cent. solution in 20 per cent. ethanol.

or

Screened methyl orange indicator solution—Dissolve 1 g of methyl orange and 1·4 g of xylene-cyanol FF in 500 ml of ethanol.

or

Bromophenol blue indicator solution—A 0·04 per cent. solution in 20 per cent. ethanol.

Phenolphthalein indicator solution—A 0·1 per cent. solution in 50 per cent. ethanol.

Hydrochloric acid solution, 0·1 N.

PROCEDURE—

Colourless or nearly colourless effluents—Remove any suspended matter from the sample by filtration or centrifuging, and transfer 100 ml of the clear liquid by pipette into a 750-ml flask, add 1 ml of phenolphthalein indicator solution and titrate with 0·1 *N* hydrochloric acid to the end-point of this indicator. Express the result as the number of millilitres of 0·1 *N* acid per litre of sample (*i.e.*, "phenolphthalein alkalinity").

To the solution neutralised to phenolphthalein add 5 drops of either solution of the methyl orange indicator or of bromophenol blue and continue the titration to the end-point. Express the sum of the two titrations in terms of millilitres of 0·1 *N* acid per litre of sample (*i.e.*, "methyl orange alkalinity").

Deeply coloured effluents—If the colour of the effluent interferes with the titration, and the interference cannot be overcome by suitable dilution with freshly boiled and cooled distilled water, an electrometric titration must be used.

NOTE—Some effluents may contain insoluble alkalinity in the form of calcium carbonate or calcium hydroxide or both. For these, the total alkalinity is determined on the unfiltered sample by adding an excess of 0·1 *N* hydrochloric acid, boiling off the carbon dioxide, cooling and titrating back to the phenolphthalein end-point with 0·1 *N* alkali.

Manganese

PRINCIPLE OF METHOD—

After destruction of the organic matter, manganese is oxidised to permanganate by means of potassium periodate in acid solution. This is then determined colorimetrically by visual comparison with standards. Instrumental measuring of the colour

of the permanganate ion is not satisfactory for concentrations of the order of 0·01 to 0·05 mg per 100 ml, but visual matching in this range is easy and reproducible.

RANGE—

For manganese contents up to 0·05 mg.

APPLICABILITY—

The method is generally applicable.

REAGENTS—

NOTE—It is essential that all reagents should be of analytical-reagent quality, since the presence of organic matter must be avoided.

Distilled water—This should be specially prepared by distilling tap water to which sulphuric acid and a few crystals of potassium permanganate have been added. Suitable precautions must be taken to exclude atmospheric dust during distillation and storage.

This specially prepared water must be used for the reagents and throughout the procedure.

Potassium periodate.

Phosphoric acid, sp.gr. 1·75.

Sulphuric acid, diluted (1 + 3).

Standard permanganate solution—Dissolve 0·288 g of potassium permanganate in 100 to 200 ml of distilled water, add 5 ml of diluted sulphuric acid and dilute the solution to 1 litre.

Dilute 10 ml of this solution to 100 ml with distilled water freshly as required.

1 ml ≡ 0·01 mg of manganese.

PROCEDURE—

Transfer a suitable aliquot (about 10 to 20 ml) of the acid solution, prepared as described under "Destruction of Organic Matter," to a beaker or flask, add 1 ml of phosphoric acid and evaporate the solution on a hot-plate to fuming. Add 75 ml of the distilled water and 1 g of solid potassium periodate; cover the vessel, boil the solution for 1 minute and then immerse the vessel in a boiling-water bath for 1 hour. Cool the solution, transfer it to a 100-ml Nessler cylinder and dilute it to the 100-ml mark. Prepare a series of standards, covering the range 0·01 to 0·05 mg of manganese, by diluting suitable aliquots of the standard permanganate solution to 100 ml in a series of matched Nessler cylinders. Determine the manganese content of the effluent by visual comparison with the standards.

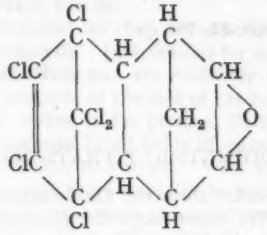
Notes

THE DETERMINATION OF MOISTURE IN DIELDRIN AND ALDRIN BY THE KARL FISCHER TITRATION METHOD

THE determination of moisture by the Karl Fischer titration method in chlorinated organic compounds used as pesticides is a well established practice. The superiority of this technique over any other for the same purpose has resulted in its adoption as the official method for the determination of moisture in technical and pure DDT, BHC, Methoxychlor and so on by the Expert Committee on Insecticides, World Health Organization.[1] The same Committee, however, recommend the use of the less accurate azeotropic-distillation technique for the determination of moisture in the newer insecticide, dieldrin. The reasons given for this were that the Karl Fischer reagent was known to react with some organic compounds and that there were no data available on its use for the determination of water content in dieldrin.

From a consideration of the molecular structure of dieldrin (**I**) and aldrin (**II**), which is closely related to it, and the information given in the literature[2] on their chemical behaviour, one would expect no interaction between the Karl Fischer reagent and dieldrin, which is already a halogenated and saturated compound. Aldrin on the other hand contains an unsaturated bond, which is known to react with halogens and other reagents to form addition products in the 6:7-positions; with phenyl azide a phenyldihydrotriazole derivative is formed, which is used as the

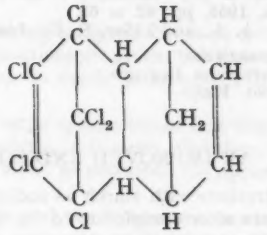
basis for the colorimetric determination of traces of aldrin,[3] and owing to this there were grounds to suspect interaction between this compound and the Karl Fischer reagent (mainly the free iodine present in the reagent).



(I)

Dieldrin

(1:2:3:4:10:10-hexachloro-6:7-epoxy-1:4:4*a*:5:6:7:8:8*a*-octahydro-1:4:5:8-*endo*, *exo*dimethanonaphthalene)



(II)

Aldrin

(1:2:3:4:10:10-hexachloro-1:4:4*a*:5:8:8*a*-hexahydro-1:4:5:8-*endo*, *exo*dimethanonaphthalene)

The titration technique used in this work was that employing the electrometric detection of the end-point (one burette system, polarised platinum electrodes with applied low e.m.f.). This was particularly advantageous with technical-grade materials containing an impurity that imparts a yellow-brown coloration to the solutions and so makes the visual end-point less distinct.

Pure and technical grades of dieldrin and aldrin (previously thoroughly dried in vacuum) were dissolved in anhydrous methanol and titrated with the Karl Fischer reagent. With each sample no reagent was consumed in excess of that needed for the solvent methanol and the end-point was sharp and stable. Then water was added, in the form of sodium acetate trihydrate, to the mixtures, which were again titrated as before. The results are shown in Table I.

TABLE I

DETERMINATION OF MOISTURE BY THE KARL FISCHER TITRATION IN PURE AND TECHNICAL DIELDRIN AND ALDRIN

Substance	Water added		Water found		Remarks
	g	%	g	%	
Dieldrin, pure, m.p. 176° C ..	0·0476	2·38	0·0473	2·37	Approximately 2·00 g of the sample were taken for each determination; 20 ml of methanol containing 0·08 per cent. of water were used as solvent
Dieldrin, technical, m.p. 130° C	0·0580	2·90	0·0586	2·93	
	0·0401	2·01	0·0398	1·99	
	0·0212	1·06	0·0216	1·08	
Aldrin, pure, m.p. 104·5° C ..	0·0573	2·87	0·0571	2·86	
Aldrin, technical, m.p. 80° C ..	0·0573	2·87	0·0571	2·86	
	0·0394	1·97	0·0395	1·98	
	0·0232	1·16	0·0235	1·18	

The results show excellent recoveries of water from admixtures with pure and technical grades of dieldrin and aldrin when determined by the Karl Fischer titration method and no interaction of the reagent, which would lead to erroneous results, with the above-named materials. The visual indication of the end-point was very satisfactory with the pure materials, which were colourless, and only slightly less satisfactory with the technical grades, owing to the yellow-brown colour imparted to the methanolic solution by the impurities, but still good enough, especially after some experience, for routine work.

I thank Plant Protection Ltd. for permission to publish this Note and Miss R. Butler and Miss A. Parker for assistance in the experimental work.

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TECHNICAL DEPARTMENT
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June 18th, 1956

AN IMPROVED END-POINT IN IODIMETRIC TITRATIONS

IODIMETRIC titrations with starch as indicator often suffer from the disadvantage that the blue colour re-appears after completion of the titration. We experienced the phenomenon of "after-blueing" in iodimetric titrations—

$$IO'_3 + 5I' + 6H^{\bullet} = 3I_2 + 3H_2O,$$

occurring in the modified Leipert[1,2] determination of iodine in organic compounds. We attributed this to the presence of traces of a contaminant, *e.g.*, iron, which will induce oxidation of iodide ions. The use of phosphoric acid instead of sulphuric acid gave an improved end-point.[3]

Two series of potassium iodide solutions containing various amounts of admixed ferric ions were prepared, and iodide ions were oxidised (*a*) by drawing air through the solution and timing the appearance of the blue colour, and (*b*) by adding known amounts of 0·1 *N* potassium iodate. Parallel experiments were carried out with sulphuric acid and phosphoric acid. We found that the minimum concentration of iron that would produce "after-blueing" in absence of phosphoric acid was about 0·1 mg of iron per 75 ml of solution.[4] The addition of 1 ml of phosphoric acid, sp.gr. 1·7, suppressed this unwanted effect and yielded quantitative results. Oxalate and fluoride ions also retarded oxidation of iodide ions in presence of admixed iron.

In view of the fact that iron is a frequent contaminant, we recommend the use of phosphoric acid instead of sulphuric acid in all iodimetric titrations when acidity is required.

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3. Suzuki, S., and Aihara, O., *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76**, 42.
4. Kolthoff, I. M., and Sandell, E. B., "Quantitative Inorganic Analysis," Macmillan & Co. Ltd., London, 1950, p. 629, Note 2.

CHEMISTRY DEPARTMENT
COLLEGE OF TECHNOLOGY
MANCHESTER, 1

B. MANOHIN
G. J. KAKABADSE
M. M. CROWDER
June 20th, 1956

British Standards Institution

NEW SPECIFICATIONS*

B.S. 1328:1956. Methods of Sampling Water used in Industry. Price 6s.
B.S. 2756:1956. Recommendations for the Use of Detergents in the Dairying Industry. Price 6s.
B.S. 2774:1956. Drawing Conventions for Laboratory Glass Apparatus. Price 3s. 6d.

AMENDMENT SLIPS*

PRINTED slips bearing amendments to British Standards have been issued by the Institution, as follows—
PD 2579—Amendment No. 1 (September, 1956) to B.S. 2736:1956. Reference Thermometers for Field Use.
PD 2581—Amendment No. 1 (October, 1956) to B.S. 2461:1954. Gas Washing Bottles.
PD 2612—Amendment No. 1 (September, 1956) to B.S. 658:1952. Apparatus for the Determination of Distillation Range.
PD 2619—Amendment No. 1 (October, 1956) to B.S. 1925:1953. Capacity of Cylindrical Glass Milk Bottles (Other than Bottles for Sterilised Milk).

* Obtainable from the British Standards Institution, Sales Department, 2 Park Street, London, W.1.

Book Reviews

ESSENTIALS OF QUANTITATIVE ANALYSIS. AN INTRODUCTION TO THE BASIC UNIT OPERATIONS. By A. A. BENEDETTI-PICHLER. Pp. xiv + 666. New York: The Ronald Press Co. 1956. Price $15.00.

Although designed for students as well as for practising analysts, this is no ordinary textbook of quantitative analysis. Instructions for some determinations are given, but these are a relatively small part of the book and are evidently intended not so much as an object in themselves as to point to the precepts of the rest of the text.

The author writes, in his preface, that with increasing specialisation it is impossible for any course to train experts in all fields of quantitative analysis; it is wiser, therefore, to concentrate on the techniques common to all. With this aim in view, he describes the apparatus and basic operations of quantitative analysis in four parts.

Part I, the introduction to quantitative analysis and the laboratory, contains a welcome chapter on errors. This will mainly be of value for reference, as the treatment is rather too brief and theoretical for a student without a grounding in statistics. Part II, about a quarter of the book, deals with measurement. Each section, on general measurement, on measurement of mass, volume, temperature, pressure, light and various physical properties related to composition, begins with an account of the historical development of the units and procedures, and describes the theory and practice of the measurements. The practising analyst, as well as the student, will find in this section much valuable material. It is surprising, however, to read that aperiodic analytical balances "cannot be generally recommended where highest precision is required," and that air-damping is dismissed as having been "successfully used."

Although short, Part III is a useful collection of data and methods in the field of laboratory technology, such as cleaning and marking apparatus, glass-blowing, grinding stop-cocks and storing and dispensing liquids. The descriptions of American apparatus will be of interest.

Analytical operations that do not involve measurement are dealt with in Part IV. Dissolving, boiling, filtering and so on receive good theoretical treatment, and there are other operations, such as sampling, centrifuging and sweeping with gases, that are not usually so fully described in textbooks of quantitative analysis. Part V is a course of experimental work for students. The instructions are generally complete and clear, but the approach, with its credits and questions and answers, will possibly find more favour in American institutions than in British. There is an Appendix with the usual, and some unusual and useful, tables, and a comprehensive and accurate Index.

The author indicates that he has adjusted the lengths of the chapters to the relative importance of their subjects. Perhaps as a result a student might find the application of some of the shorter chapters rather obscure, while regarding a few other sections as unnecessarily detailed. This criticism of unevenness is put in perspective, however, by the enormous amount of useful description and discussion provided.

The book is well produced, the references are up to date and the diagrams are excellent.

D. W. WILSON

REAGENT CHEMICALS AND STANDARDS. BY JOSEPH ROSIN. Third Edition. Pp. x + 561. D. Van Nostrand Co. Inc.; New York: London: Macmillan & Co. Ltd. 1955. Price $9.50; 70s.

THE First Edition of this work was reviewed in *The Analyst*, 1937, **62**, 832. The earlier specifications appear to have undergone little change, but additional substances have been introduced to increase the number from 474 to more than 600, 45 being new to the Third Edition. The author directs attention to the following additions: anthrone, *cyclo*hexane, dimethylformamide, ethylenediaminetetra-acetic acid, Eriochrome black T, *iso*octane, rhodamine B, tetramethylammonium hydroxide, triphenyltetrazolium chloride and vanadyl sulphate.

Most potassium salts are tested for sodium, but it is surprising to find that a simple visual flame test is used ("no distinct yellow colour") with a platinum wire, considering especially that quantitative limits (albeit on an approximate basis) have been correlated with these tests. The flame photometer is now in common use and would have served this purpose so much better. The method of testing benzene for thiophen is most insensitive; the isatin should be added to the sulphuric acid before it is shaken with the benzene.

The book contains rather more misprints than should be expected, but, apart from these, the production is of a very high quality, and the third edition will certainly rank with its predecessors as a standard work on the subject.

W. C. JOHNSON

Publications Received

ORGANIC CHEMISTRY. Volume II. STEREOCHEMISTRY AND THE CHEMISTRY OF NATURAL PRODUCTS. By I. L. FINAR, B.Sc., Ph.D., A.R.I.C. Pp. xii + 733. London, New York and Toronto: Longmans, Green & Co. Ltd. 1956. Price 40s.

HYDROGEN IONS: THEIR DETERMINATION AND IMPORTANCE IN PURE AND INDUSTRIAL CHEMISTRY. Volume II. By H. T. S. BRITTON, D.Sc., D.I.C., F.R.I.C. Fourth Edition. Pp. xx + 489. London: Chapman & Hall Ltd. 1956. Price 75s.

INTRODUCTION TO STRUCTURE IN ORGANIC CHEMISTRY. By C. K. INGOLD, D.Sc., F.R.S. Pp. viii + 200. London: G. Bell & Sons Ltd. 1956. Price 20s.

METALLURGICAL ANALYSIS BY MEANS OF THE SPEKKER PHOTOELECTRIC ABSORPTIOMETER. By F. W. HAYWOOD, B.Sc., Ph.D., F.R.I.C., F.I.M., and A. A. R. WOOD, A.R.I.C. Second Edition. Pp. viii + 292. London: Hilger & Watts Ltd. 1956. Price 40s.

CANNED FOODS: AN INTRODUCTION TO THEIR MICROBIOLOGY. By J. G. BAUMGARTNER and A. C. HERSOM, B.Sc., A.R.I.C. Fourth Edition. Pp. vi + 291. London: J. & A. Churchill Ltd. 1956. Price 21s.

MICRO-ANALYSIS IN MEDICAL BIOCHEMISTRY. By E. J. KING, M.A., Ph.D., D.Sc., F.R.I.C., and I. D. P. WOOTTON, Ph.D., M.A., M.B., B.Chir., F.R.I.C. Third Edition. Pp. xii + 292. London: J. & A. Churchill Ltd. 1956. Price 22s. 6d.

CLINICAL CHEMISTRY: PRINCIPLES AND PROCEDURES. By JOSEPH S. ANNINO. Pp. xxii + 280. London: J. & A. Churchill Ltd.; Boston and Toronto: Little, Brown & Co. 1956. Price 54s.; $7.50.

THE CONDENSED CHEMICAL DICTIONARY. Fifth Edition. Revised by ARTHUR and ELIZABETH ROSE. Pp. xx + 1201. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1956. Price $12.50; 100s.

RECOMMENDED METHODS FOR THE ANALYSIS OF TRADE EFFLUENTS

REPRINTS of the Recommended Methods prepared by the Joint A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents that were published in the January, March and August, 1956, issues of *The Analyst* are now available from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1; price to members 1s. 6d., or to non-members 2s. 6d. Remittances made out to The Society for Analytical Chemistry must accompany orders, and these reprints are not available through Trade Agents. The subjects covered are as follows—

Reprint No. 1. Preparation of Sample *and* Determination of Arsenic and Copper.
Reprint No. 2. Determination of Iron, Mercury and Nickel.
Reprint No. 3. Sampling and Physical Examination of the Sample.

Erratum

OCTOBER (1956) ISSUE, p. 593, 4th line from foot of page. *For* "ε-Aminocaproic acid dihydrochloride" *read* "Hexamethylenediamine dihydrochloride."